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(54) Title: HOMOPOLYMERS AND COPOLYMERS OF ETHYLENE

(57) Abstract

Ethylene homopolymers and copolymers having a broad molecular distribution, excellent toughness and improved processability are disclosed. These polymers may be prepared by use of a single metallocene catalyst system in a single reactor in the gas phase. These polymers of density typically 0.85–0.95 are defined in particular by their melt strength (MS) and long chain branching (LCB) characteristics and are particularly suitable for use in low density film applications.

HOMOPOLYMERS AND COPOLYMERS OF ETHYLENE

The present invention relates to novel polymers and in particular to novel copolymers having a broad molecular weight distribution, toughness and improved processability.

In recent years there have been many advances in the production of
5   polyolefin copolymers due to the introduction of metallocene catalysts. Metallocene catalysts offer the advantage of generally higher activity than traditional Ziegler catalysts and are usually described as catalysts which are single-site in nature. Because of their single-site nature the polyolefin copolymers produced by metallocene catalysts often are quite uniform in their molecular
10   structure. For example, in comparison to traditional Ziegler produced materials, they have relatively narrow molecular weight distributions (MWD) and narrow Short Chain Branching Distribution (SCBD). Although certain properties of metallocene products are enhanced by narrow MWD, difficulties are often encountered in the processing of these materials into useful articles and films
15   relative to Ziegler produced materials. In addition, the uniform nature of the SCBD of metallocene produced materials does not readily permit certain structures to be obtained.

An approach to improving processability has been the inclusion of long chain branching (LCB), which is particularly desirable from the viewpoint of
20   improving processability without damaging advantageous properties. US Patent No.s 5,272,236; 5,278,272; 5,380,810; and EP 659,773, EP 676,421, relate to the production of polyolefins with long chain branching.

Another approach is the addition of the polymer processing aids to the polymer prior to fabrication into films or articles. This requires extra processing
25   and is expensive.

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A different approach to the problem has been to make compositions which are blends or mixtures of individual polymeric materials with the aim being to maximise the beneficial properties of given component while minimising its processing problems. This also requires extra processing which increases the cost

5   of materials produced. US Patent No.'s 4,598,128; 4,547,551; 5,408,004; 5,382,630; 5,383,631; and 5,326,602; and WO 94/22948 and WO 95/25141 relate to typical blends.

Another way to provide a solution for the processability problems and to vary SCBD has been the development of various cascade processes, where the

10 material is produced by a series of polymerizations under different reactor conditions, such as in a series of reactors. Essentially, a material similar in some ways to a blend is produced, with a modality greater than one for various physical properties, such as the molecular weight distribution. While polyolefin compositions with superior processability characteristics can be produced this way,

15 these methods are expensive and complicated relative to the use of a single reactor. Processes of interest are disclosed in US Patent No. 5,442,018, WO 95/26990, WO 95/07942 and WO 95/10548.

Another potentially feasible approach to improving processability and varying SCBD has been to use a multicomponent catalyst. In some cases, a

20 catalyst which has a metallocene catalyst and a conventional Ziegler-Natta catalyst on the same support are used to produce a multimodal material. In other cases two metallocene catalysts have been used in polyolefin polymerizations. Components of different molecular weights and compositions are produced in a single reactor operating under a single set of polymerisation conditions. This approach is difficult

25 from the point of view of process control and catalyst preparation. Catalyst systems of interest are disclosed in WO 95/11264 and EP 676,418.

WO96/04290 teaches the use of the preferred metallocene complexes of this invention to make ethylene copolymers. In particular, Examples 44 and 45 teach the preparation of polymer using gas-phase techniques. The examples teach

30 only operation for a hour or less in batch mode and no details of the original polymer bed composition is given.

US 5462999 and US 5405922 teaches the preparation of ethylene copolymers in the gas-phase using a silica supported metallocene catalyst. It is believed, however, that the products produced by following the examples will not

35 contain long chain branching and in particular will have lower values for the

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parameters $\delta(MS)/\delta(P)$ and $\delta(MS)/\delta(\log \dot{y})$ than is claimed herein.

EP 676421 also teaches the preparation of copolymers in the gas phase using a supported metallocene catalyst. The products produced in the examples of this patent in general also have lower values for the parameters $\delta(MS)/\delta(P)$ and
5 $\delta(MS)/\delta(\log \dot{y})$ than is claimed herein.

EP 452920 and EP495099 teach the production of ethylene copolymers using metallocene catalysts. Once again it is believed that the examples contained therein will not produce products with some or all of the desirable characteristics mentioned below

10 It would be desirable to be able to produce a polyolefin copolymer composition which is very easy to process and which is produced using a single metallocene catalyst system preferably supported in a polymerisation process using a single reactor, preferably gas phase, operating semi-continuously or, preferably, continuously under a single set of reactor conditions.

15 It would also be desirable to produce polymers which have the processability and impact strength similar to highly branched low density polyethylene (LDPE).

It would also be highly desirable to produce polymers having the above properties which may be suitable for use in low density polyethylene film
20 applications.

We have now found copolymers of ethylene and alpha olefins may be prepared which have improved processability and which exhibit specific melt strength characteristics. Such copolymers are advantageously prepared using a single metallocene catalyst system using a single gas-phase, fluidised bed reactor.

25 Thus according to a first aspect of the present invention there is provided a copolymer of ethylene and one or more alpha olefins containing from three to twenty carbon atoms said copolymer having:-

a) a long chain branching g' value of less than or equal to 0.9 and

b) a value of the derivative function $\delta(MS)/\delta(P)$ of greater than 0.6
30 wherein MS is the melt strength of the copolymer in cN and P is the extrusion pressure of the copolymer in MPa.

In a second aspect of the invention there is provided a copolymer of ethylene and one or more alpha olefins containing from three to twenty carbon atoms said copolymer having:

35 a) a long chain branching g' value of less than or equal to 0.9 and

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b)   a value of the derivative function $\delta(MS)/\delta(\log\dot\gamma)$ of greater than 7.5 wherein MS is the melt strength of the copolymer in cN and $\dot\gamma$ is the shear rate of the copolymer in secs^{-1}.

Also provided by the present is a homopolymer of ethylene or a copolymer of ethylene and one or more alpha olefins containing from three to twenty carbon atoms said homopolymer or copolymer having:

a)   a value of the derivative function $\delta(MS)/\delta(P)$ of greater than 0.6 and

b)   an M_w/M_n value of in the case of the copolymer less than 8 and in the case of the homopolymer less than 6

wherein MS is the melt strength of the copolymer or homopolymer in cN and P is the extrusion pressure of the copolymer or homopolymer in MPa and M_w/M_n is the ratio of weight average molecular weight to number average molecular weight of the copolymer or homopolymer as measured by gel permeation chromatography.

The derivative function value $\delta(MS)/\delta(P)$ is preferably ≥ 0.75 and more preferably ≥ 0.8.

In a further aspect of the present invention as herein described there is provided a homopolymer of ethylene or a copolymer of ethylene and one or more alpha olefins containing from three to twenty carbon atoms said homopolymer or copolymer having:

a)   a value of the derivative function $\delta(MS)/\delta(\log\dot\gamma)$ of greater than 7.5 and

b)   an M_w/M_n value of less than 6.5

wherein MS is the melt strength of the copolymer in cN and $\dot\gamma$ is the shear rate of the copolymer in secs^{-1} and M_w/M_n is the ratio of weight average molecular weight to number average molecular weight as measured by gel permeation chromatography.

Another aspect of the present invention is provided by a homopolymer of ethylene or a copolymer of ethylene and one or more alpha olefins containing from three to twenty carbon atoms said homopolymer or copolymer having a long chain branching g' value of between about 0.6 and about 0.9. The homopolymers and copolymers of this aspect of the invention may also have either or both of (a) a value of the derivative function $\delta(MS)/\delta(P)$ of greater than 0.6 or (b) a value of the derivative function $\delta(MS)/\delta(\log\dot\gamma)$ of greater than 7.5 wherein MS is the melt strength of the copolymer in cN and P is the extrusion pressure of the copolymer in MPa and $\dot\gamma$ is the shear rate of the copolymer in secs^{-1}.

The homopolymers and copolymers of the present invention which are

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described above exhibit considerable rate advantages when processed for commercial use. Thus relative to those products known to date the homopolymers and copolymers of the present invention can be processed at lower melt temperature with lower melt pressure and lower power consumption than for

5   previously known polymers of equivalent melt index. Alternatively for the same external conditions higher throughputs can be achieved.

The long chain branch parameter, g' may be calculated from gel permeation chromatography data (GPC) on-line viscometry data.

Although the present invention is not limited in all its aspects to

10   homopolymers and copolymers possessing long chain branches, it is preferable that all the homopolymers and copolymers of the present invention have this feature. In such cases, the value of the long chain branching parameter g' for all the copolymers of the present invention should be less than 0.9, preferably less than 0.8, or alternatively preferably greater than 0.5. Preferably the parameter lies in the

15   range about 0.5 to about 0.9 preferably in the range 0.55 to 0.85 more preferably in the range about 0.6 to about 0.8 and most preferably in the range 0.65 to 0.8. For the homopolymers the g' parameter should be in the range about 0.6 to about 0.9 more preferably 0.6 to 0.8 and most preferably 0.65 to 0.8.

As far as the melt strength (MS), extrusion pressure (P) and shear rate $(\dot{\gamma})$

20   parameters are concerned, the methods of measuring these for polymers are well known to those skilled in the art. By measuring the MS parameter it is possible to construct for example graphical relationships which allow the two derivative functions $\delta(MS)/\delta(P)$ and $\delta(MS)/\delta(\log\dot{\gamma})$ to be calculated. The melt strength (MS) and extrusion pressure at shear rate of 500/S may also be calculated in this way.

25   Although the present invention is not limited in all its aspects to homopolymers and copolymers in which either or both of these derivative functions is a critical parameter, it is preferable that all the homopolymers and copolymers of the present invention meet at least one and preferably both of the following numerical constraints. As far as the derivative function $\delta(MS)/\delta(P)$ is concerned this should

30   be greater than 0.6, desirably greater than 0.65, more desirably greater than 0.7 and most desirably greater than 0.80. Preferably the value of the derivative function $\delta(MS)/\delta(P)$ should be in the range greater than 0.6 to less than 1.5 more preferably from 0.65 to less than 1.4, even more preferably from 0.7 to 1.3 and most preferably from 0.8 to 1.2.

35   The derivative function $\delta(MS)/\delta(\log\dot{\gamma})$ should be greater than 7.5 desirably

7.75 or greater and more desirably 8.0 or greater. Preferably the value of this derivative function lies in the range greater than 7.5 to 15.0, more preferably from 7.75 to 13.0 and most preferably 8.0 to 12.0.

The copolymers according to the present invention may also be defined

5   with respect to activation energy Ea as measured by dynamic rheometry. Thus according to another aspect of the invention there is provided a copolymer of ethylene and one or more alpa olefins containing from three to twenty carbon atoms said copolymer having:-

(a) an activation energy, Ea, of value greater than or equal to 40 kJ/mol and

10   (b) a value of the derivative function $\delta(MS)/\delta(P)$ of greater than 0.6 wherein MS is the melt strength of the copolymer in cN and P is the extrusion pressure of the copolymer in MPa. Ea is measured by dynamic rheometry.

Preferably the value of the derivative function $\delta(MS)/\delta(P)$ is greater than 0.65 and most preferably greater than 0.75.

15   The derivative function may also be represented by the relationship

$$0.65 \leq \delta(MS)/\delta(P) \leq 1.4$$

and preferably

$$0.7 \leq \delta(MS)/\delta(P) \leq 1.2.$$

In a further aspect of the invention there is provided a copolymer of

20   ethylene and one or more alpa olefins containing from three to twenty carbon atoms said copolymer having:-

(a) an activation energy, Ea of value greater than or equal to 40 kJ/mol and

(b) a value of the derivative function $\delta(MS)/\delta(\log \dot{\gamma})$ of greater than 7.5 wherein MS is the melt strength of the copolymer in cN and γ is the shear rate of

25   the copolymer in $\sec^{-1}$. Ea is measured by dynamic rheometry.

Preferably the value of the derivative function $\delta(MS)/\delta(\log \dot{\gamma})$ is greater than 7.5 and most preferably greater than 8.0.

The derivative function may also be represented by the relationship

$$8.0 \leq \delta(MS)/\delta(\log \dot{\gamma}) \leq 12.$$

30   In normal polymer extrusion, for example in film processing, the throughput rate is usually high and the corresponding shear rate is expected to be in region of, or greater than, 500 /s. The shear viscosity $\eta(500 /s)$, extrusion pressure $P(500 /s)$ and melt strength $MS(500 /s)$, measured at shear rate of 500 /s, using both the capillary rheometer and Rheotens, have thus been used to

35   characterise the processability of polymer (Table 2). Although the present

invention is not limited in all its aspects to homopolymers and copolymers in which these parameters are critical, it is preferable that all the homopolymers and copolymers of the present invention should have a MS(500 /s) be greater than 13 cN desirably 15 cN and more desirably 16 cN or greater; a P(500 /s) value should

5   be less than or equal to 19 MPa desirably 18 MPa and more desirably 17.5 MPa or less; a η(500 /s) should be less than or equal to 430 Pa.s desirably 400 Pa.s and more desirably 300 Pa.s or less.

In another aspect of the invention there is provided a copolymer of ethylene and one or more alpha olefins containing from three to twenty carbon atoms said

10 copolymer having:-

(a) a long chain branching g' value of less than or equal to 0.9 and

(b) a melt strength, MS(500 /s) and extrusion pressure, P(500 /s) satisfying the relationship:

$$MS(500 /s) > \text{or} = P(500 /s) - 4.5$$

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$$MS(500 /s) > \text{or} = P(500 /s) - 4 \text{ desirably}$$

$$MS(500 /s) > \text{or} = P(500 /s) - 3.5 \text{ more desirably}$$

wherein MS is the melt strength of the copolymer in cN and P is the extrusion pressure of the copolymer in MPa, all determined at shear rate of 500 /s using a Rosand Capillary Rheometer and a Göttfert Rheotens.

20 In a further aspect of the invention there is provided a copolymer of ethylene and one or more alpha olefins containing from three to twenty carbon atoms said copolymer having:-

(a) an activation energy, Ea, of value greater than or equal to 40 kJ/mol and

(b) a melt strength, MS(500 /s) and extrusion pressure, P(500 /s) satisfying

25 relationship:

$$MS(500 /s) > \text{or} = P(500 /s) - 4.5$$

$$MS(500 /s) > \text{or} = P(500 /s) - 4 \text{ desirably}$$

$$MS(500 /s) > \text{or} = P(500 /s) - 3.5 \text{ more desirably}$$

wherein MS is the melt strength of the copolymer in cN and P is the extrusion

30 pressure of the copolymer in MPa, all determined at shear rate of 500 /s using a Rosand Capillary Rheometer and a Göttfert Rheotens. Ea is measured by dynamic rheometry.

Another aspect of the invention there is provided a copolymer of ethylene and one or more alpha olefins containing from three to twenty carbon atoms said

35 copolymer having:-

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(a) a melt strength, MS(500 /s) and Mw/Mn value satisfying relationship:

$$MS(500\text{ /s}) > \text{or} = 1.13\ (Mw/Mn) + 9.5, \text{ and}$$

(b) a melt strength, MS(500 /s) and extrusion pressure, P(500 /s) satisfying relationship:

$$MS(500\text{ /s}) > \text{or} = P(500\text{ /s}) - 4.5$$

$$MS(500\text{ /s}) > \text{or} = P(500\text{ /s}) - 4 \text{ desirably}$$

$$MS(500\text{ /s}) > \text{or} = P(500\text{ /s}) - 3.5 \text{ more desirably}$$

wherein MS is the melt strength of the copolymer in cN and P is the extrusion pressure of the copolymer in MPa, all determined at shear rate of 500 /s using a Rosand Capillary Rheometer and a Göttfert Rheotens. Mw/Mn is the ratio of weight average molecular weight to number molecular weight as measured by gel chromatography.

Another aspect of the invention there is provided a copolymer of ethylene and one or more alpha olefins containing from three to twenty carbon atoms said copolymer having:-

(a) a melt strength, MS(500 /s) and Mw/Mn value satisfying relationship:

$$MS(500\text{ /s}) > \text{or} = 1.13\ (Mw/Mn) + 9.5, \text{ and}$$

(b) a melt strength, MS(500 /s) and shear viscosity, η(500 /s) satisfying relationship:

$$MS(500\text{ /s}) > \text{or} = 0.053\ \eta(500\text{ /s}) - 4.0$$

$$MS(500\text{ /s}) > \text{or} = 0.053\ \eta(500\text{ /s}) - 3.5 \text{ desirably}$$

$$MS(500\text{ /s}) > \text{or} = 0.053\ \eta(500\text{ /s}) - 3.0 \text{ more desirably}$$

wherein MS is the melt strength of the copolymer in cN and η is the shear viscosity of the copolymer in Pa.s, all determined at shear rate of 500 /s using a Rosand Capillary Rheometer and a Göttfert Rheotens. Mw/Mn is the ratio of weight average molecular weight to number molecular weight as measured by gel chromatography.

The parameter M_w/M_n is calculated from corresponding values for the weight average molecular weight M_w and the number average molecular weight M_n in turn obtained from gel permeation chromatography. Although the present invention is not limited in all its aspects to homopolymers and copolymers in which this parameter is critical, it is preferable that all the homopolymers and copolymers of the present invention should have an M_w/M_n value of less than 8 preferably less than 7 more preferably less than 6.5 and most preferably less than 6.

Turning to other characteristics of the homopolymers and copolymers of

the present invention, the density of these materials should be in the range 0.8 to 1.0 preferably 0.85 to 0.95 and most preferably 0.91 to 0.93. It is preferable that the melt flow ratio of the polymer measured at a load of 2.16 kg by standard techniques is in the range 0.01 to 100 and more preferably in the range 0.1 to 10

5   dg.min^{-1}. Typically the weight average molecular weight of the material is in the range 25,000 to 500,00 preferably 50,000 to 250,000 and most preferably 80,000 to 200,000. For the copolymers of the present invention it is preferable that they are comprised of between 2 and 30 weight %, most preferably between 5 and 20 weight % of units derived from the precursor comonomer.

10   The most preferable homopolymers and copolymers of the present invention appear to be characterised by molecular weight distributions (as measured by gel permeation chromatography) which show varying degrees of deviation from unimodality. In some instances these non unimodal characteristics are manifested in clear bimodality or even more complex distributions indicative of

15   even higher orders of modality. This property is one which in particular has been seen before in connection with single site catalyst operating in a single reaction environment.

The homopolymers and copolymers of the present invention are suitably prepared by continuous polymerisation of the required monomer(s) in the presence

20   of a single metallocene catalyst system in a single reactor. By the term continuous polymerisation is meant a process which for at least a significant period of time is operated with continuous feeding of the monomer(s) to the reactor in parallel with continuous or periodic withdrawing of homopolymer or copolymer product. Preferably the continuous polymerisation is effected in the gas phase at elevated

25   temperature in the presence of a fluidised bed of polymer particles and continuous recycle of unreacted monomer(s) around a loop joining the inlet and outlet of the reactor containing the fluidised bed. Examples of two possible approaches are described in EP 89961, US 53527947 and US 5541270 the complete texts of which are herein incorporated by reference. EP 699213 also illustrates a possible

30   approach and again the complete text of this publication is incorporated by reference. The metallocene catalyst system comprises a metallocene complex and activating cocatalyst which in the case of a gas phase process is preferably supported on an inert carrier (e.g. silica). The catalyst system can be optionally prepolymerised and/or utilised in the presence of a Group IIIa metal alkyl

35   scavenger such as an aluminium alkyl.

Suitable metallocene complexes which can be used to prepare the homopolymers and copolymers of the present invention comprise those organometallic complexes of the Group IVB (i.e. the titanium group) having between one and three η^5 bonded cylopentadienyl indenyl or fluorenyl ligands.

5   Whilst these ligands may be unsubsituted or substituted at one or more of their carbon atoms with a substituent, including but not limited to alkyl groups having from one and ten carbon atoms, the most preferred metallocene complexes are those where at least two of the cyclopentadienyl, indenyl and fluorenyl ligands are connected together by a divalent bridging group e.g. an alkylene group having from

10   one to eight carbon atoms or the corresponding silylene, germanylene derivatives. These alkylene, silylene and germanylene groups can in turn be substituted on the carbon and silicon backbone. Alternatively bridging can be effected by using a divalent phoshino or amino group the third valence of each being satisfied by an alkyl group having between one and eight carbons or phenyl (either substituted or

15   unsubstituted).

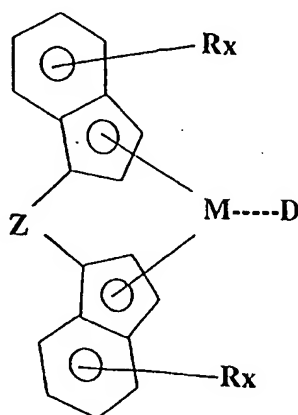The indenyl or fluorenyl ligands in such complexes may also be in the form of their hydrogenated derivatives.

Most preferred metallocene complexes are those having the following general formula:

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wherein

M is titanium, zirconium or hafnium,

D is a stable conjugated diene optionally substituted with one or more

35   hydrocarbyl groups, silyl groups, hydro carbylsily groups, silylhydrocarbyl groups

or mixtures thereof, or may contain a Lewis base functionality, said D having from 4 to 40 non-hydrogen atoms and forming a π- complex with M,

Z is a bridging group comprising an alkylene group having 1-20 carbon atoms or a dialkyl silyl- or germanyl group or alkyl phosphine or amino radical,

5   R is hydrogen or alkyl having from 1-10 carbon atoms, and x is 1-6.

Most preferred metallocene complexes in this family are those where, as evidenced by X-ray diffraction or NMR, the D ligand is π-bonded to the M atom in an η^3 fashion. Such metallocene complexes are characterised by the M atom being in the +2 oxidation state.

10   Preferred complexes are those wherein M is zirconium and Z is ethylene (CH_2CH_2).

The D ligand is most preferably chosen from the group:

s-trans-η^4,4-diphenyl-1,3-butadiene; s-trans-η^4-3-methyl-1,3-pentadiene; s-trans-η^4-1,4-dibenzyl-1,3-butadiene; s-trans-η^4-2,4-hexadiene; s-trans-η^4-1,4-

15   ditolyl-1,3-butadiene; s-trans-η^4-1,4-bis(trimethylsilyl)-1,3-butadiene; scis-η^4- 1,4-diphenyl-1,3-butadiene; s-cis-η^4-3-methyl-1,3-pentadiene; s-cis-η^4-2,4-hexadiene; s-cis-$\eta^4$2,4-hexadiene; s-cis-$\eta^4$1,3-pentadiene; s-cis-η^4-1,4-ditolyl-1,3-butadiene; and s-cis-η^4-1,4-bis(trimethylsilyl)-1,3-butadiene, said s-cis diene group forming a π-complex as defined herein with the metal.

20   Particularly suitable are externally substituted dienes in particular the 1,4-diphenyl substituted butadienes.

The preparation of these complexes is extensively described in WO 96/04290 which also lists examples of suitable representatives for use in the present invention.

25   When the diene group D has a Lewis base functionality this may be chosen from the following groups:
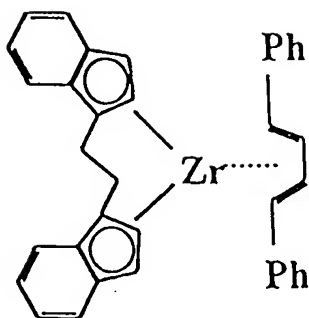
- NR_2, -PR_2, - AsR_2, - OR, - SR

Particularly preferred dienes of this type are dialkylamino phenyl substituted dienes for example 1-phenyl - 4 (N,N^1 - diethylamino phenyl) 1,3-butadiene.

30   The most preferred complex is ethylene bis(indenyl) zirconium (II) 1,4-diphenyl butadiene having the following formula:-

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10   Also preferred is the hydrogenated analogue - ethylene
bis(tetrahydroindenyl) zirconium (II) 1,4-diphenyl butadiene.

          The activating cocatalysts suitable for use with the above metallocene
complexes are preferably tri(hydrocarbyl) boranes in particular trialkylboranes or
triarylboranes. Most preferred cocatalysts are perfluorinated tri(aryl) boron

15   compounds and most especially tris(pentafluorophenyl) borane. Other activators
include borate salts of a cation which is a Bronsted acid capable of donating a
proton to one of the ligands on the metallocene complex. The potential scope of
both these types of activators is illustrated in WO 96/04290.the relevant sections of
which are herein incorporated by reference.

20   Another type of activator suitable for use with the metallocene complexes
of the present invention are the reaction products of (A) ionic compounds
comprising a cation and an anion wherein the anion has at least one substituent
comprising a moiety having an active hydrogen and (B) an organometal or
metalloid compound wherein the metal or metalloid is from Groups 1-14 of the

25   Periodic Table.

          Suitable activators of this type are described in WO 98/27119 the relevant
portions of which are incorporated by reference.

          A particular preferred activator of this type is the reaction product obtained
from alkylammonium tris(pentafluorophenyl) 4-(hydroxyphenyl) borates and

30   trialkylamines. For example a preferred activator is the reaction product of
bis(hydrogenated tallow alkyl) methyl ammonium tris (pentafluorophenyl) (4-
hydroxyphenyl) borate and triethylamine.

          The molar ratio of metallocene complex to activator employed in the
process of the present invention may be in the range 1:10000 to 100:1. A

35   preferred range is from 1:5000 to 10:1 and most preferred from 1:10 to 10:1.

The metallocene catalysts system suitable for use in the present invention is most suitably supported. Typically the support can be any organic or inorganic inert solid. However particularly porous supports such as talc, inorganic oxides and resinous support materials such as polyolefins which have well-known

5   advantages in catalysis are preferred.. Suitable inorganic oxide materials which may be used include Group 2, 13, 14 or 15 metal oxides such as silica, alumina, silica-alumina and mixtures thereof. Other inorganic oxides that may be employed either alone or in combination with the silica, alumina or silica-alumina are magnesia, titania or zirconia. Other suitable support materials may be employed

10 such as finely divided polyolefins such as polyethylene.

The most preferred support material for use with the supported catalysts according to the process of the present invention is silica. Suitable silicas include Crossfield ES70 and Davidson 948 silicas.

It is preferable that the silica is dried before use and this is typically carried

15 out by heating at elevated temperatures for example between 200 and 850 deg. C.

In another aspect of the present invention homopolymers of ethylene or copolymers of ethylene and one or more alpha-olefins containing from three to twenty carbon atoms may be prepared in the presence of a single metallocene catalyst comprising a metallocene complex and an activating cocatalyst wherein the

20 activating cocatalyst is not an alkyl aluminoxane for example methyl aluminoxane (MAO).

In such cases there is thus provided a copolymer of ethylene and one or more alpha-olefins containing from three to twenty carbon atoms said copolymer having:-

25   (a) a long chain branching g' value of less than or equal to 0.9 and

(b) a value of the derivative function $\delta(MS)/\delta(\log \dot{\gamma})$ and a Mw/Mn satisfy the relationship:

$$\log [\delta(MS)/\delta(\log \dot{\gamma})] \geq 0.6 \log (Mw/Mn) + 0.3$$

wherein Mw/Mn is the ratio of weight average molecular weight to number

30 molecular weight as measured by gel chromatography.

Such polymers may also be defined by:-

(a) a long chain branching g' value of less than or equal to 0.9 and

(b) a value of the derivative function $\delta(MS)/\delta(P)$ and Mw/Mn which satisfy the relationship:

35      $$\delta(MS)/\delta(P) \geq 0.12 \ Mw/Mn$$

wherein Mw/Mn is the ratio of weight average molecular weight to number molecular weight as measured by gel chromatography.

The polymers may also be defined with respect to the flow activation energy Ea as follows:-

5   (a) an flow activation energy, Ea, of value greater than or equal to 40 kJ/mol and

     (b) a value of the derivative function $\delta(MS)/\delta(\log \dot{\gamma})$ and a Mw/Mn which satisfy the relationship:

$$\log [\delta(MS)/\delta(\log \dot{\gamma})] \geq 0.6 \log (Mw/Mn) + 0.3$$

10 wherein Mw/Mn is the ratio of weight average molecular weight to number molecular weight as measured by gel chromatography. Ea is measured by dynamic rheometry. Alternatively the polymers may be defined by:

     (a) an flow activation energy, Ea, of value greater than or equal to 40 kJ/mol and

15   (b) a value of the derivative function $\delta(MS)/\delta(P)$ and Mw/Mn which satisfy the relationship:

$$\delta(MS)/\delta(P) \geq 0.12 \, Mw/Mn$$

wherein Mw/Mn is the ratio of weight average molecular weight to number molecular weight as measured by gel chromatography. Ea is measured by dynamic

20 rheometry.

The polymer may be defined by:

(a)   a long chain branching g' value of less than or equal to 0.9 and

(b)   a value of the derivative function $\delta(MS)/\delta(P)$ and a flow activation energy Ea satisfy the relationship:

25      $$\text{Log} [\delta(MS)/\delta(P)] \geq 3.7 - 2.4 \log (Ea)$$

wherein Ea is measured by dynamic rheometry.

Such polymers may also be defined by:

(a)   a long chain branching g' value of less than or equal to 0.9 and

(b)   a value of the derivative function $\delta(MS)/\delta(\log \dot{\gamma})$ and a flow activation

30 energy Ea satisfy the relationship:

$$\text{Log} [\delta(MS)/\delta(\log \dot{\gamma})] \geq 2.75 - 1.25 \log(Ea)$$

wherein Ea is measured by dynamic rheometry.

The copolymers of the present invention are copolymers of ethylene with one or more alpha-olefins having from three to twenty carbon atoms. Preferably

35 the alpha-olefin has between three and ten carbon atoms most preferably three and

eight. Examples of the most preferred alpha olefins include l-butene, l-hexene, 4-methyl-l-pentene, l-octene. Particular suitable are copolymers of ethylene with l-hexene or 4-methyl-1-pentene.

Fabricated articles made from the novel polymers of the present invention may be prepared using conventional polyolefin processing techniques. Suitable articles of this type include film (eg cast, blown etc) fibres and moulded articles (eg produced using injection moulding, blow moulding or rotomoulding processes).

Other useful compositions are also possible comprising the novel polymers of the present invention and at least one other natural or synthetic polymer. Such compositions may be formed by conventional methods for example dry blending. Other suitable processing techniques may be used to prepare such compositions comprising the novel polymers of the present invention.

The novel polymers of the present invention may suitably be used for the manufacture of films and specific details of the film properties and given below in the examples.

In particular the novel polymers of the present invention may be used to prepare films having a dart impact value as measured by ASTM D1709 (method A) of greater than 100 and up to about 2000. Such films comprise copolymers of the invention of density 0.910 - 0.930, a I_{21}/I_2 value of $\geq$ 35 and a long chain branching g^1 value of less than or equal to 0.9. In addition the copolymers exhibit the melt strength characteristics defined in detail above.

In particular they exhibit a value of the derivative function $\delta(MS)/\delta(P)$ of $>$ 0.6. Alternatively they may also exhibit a value of the derivative function $\delta(MS)/\delta(P)$ and flow activation Ea of

$$\log[\delta(MS)/\delta(P)] \geq 3.7 - 2.4 \log Ea.$$

Such polymers also exhibit a flow activation Ea of $\geq$ 40.

The present invention will now be further illustrated with reference to the following examples and Figures which represent the preparation of copolymers according to the present invention and a comparison with commercially available prior art materials.

Figure 1 shows the variation in melt strength (MS) with extrusion pressure at 190°C.

Figure 2 shows the variation in melt strength (MS) with shear rate at 190°C.

Figure 3 shows the variation in $\delta(MS)/\delta(P)$ with melt flow rate (2.16Kg) at

190°C

Figure 4 shows the variation in $\delta(MS)/\delta(\log\dot\gamma)$ with melt flow rate (2.16Kg) at 190°C.

Figure 5 shows the variation in $\delta(MS)/\delta(P)$ with M_w/M_n at 190°C

Figure 6 shows the variation in the $\delta(MS)/\delta(\log\dot\gamma)$ with M_w/M_n at 190°C

Figure 7 shows the variation in $\delta(MS)/\delta(P)$ with the long chain branching parameter g′ at 190°C.

Figure 8 shows the variation in $\delta(MS)/\delta(\log\dot\gamma)$ with the long chain branching parameter g′ at 190°C.

Figure 9 shows the variation in $\delta(MS)/\delta(P)$ with flow activation energy (Ea) at 190°C.

Figure 10 shows the variation in $\delta(MS)/\delta(\log\dot\gamma)$ with flow activation energy (Ea) at 190°C.

Table 2 sets out a range of relevant physical information for seven examples according to the present invention and examples of eleven commercially available or representative prior art materials.

The terms 'Exceed', 'Affinity', and 'Dowlex' are registered trade marks and herein recognised as such. Affinity FM1570, Exceed ML27MAX, Exceed 350D60, Dowlex 2045, NTA 101, LL7206AF, LL7209AA, LD 5320AA, LD 5310AA, and Borealis LE 65 92 are all commercially available products whose origin will be known to those skilled in the art. EBI/Zr(IV)/MAO is an experimental material produced according to EP 676421.

The following analytical procedures were used in order to characterise the novel polymers of the present invention and to compare said polymers with the prior art and commercially available materials.

1.   **Rheological Characterisation**

1.1   **Capillary Rheometry**

The shear capillary viscosities of the polymers were measured at 190°C, using a Rosand RH 7 twin-bore capillary rheometer, with two 1.0 mm diameter dies: one with die length of 16 mm while the other has a (zero) die length of 0.25 mm. The die entry angle for both dies is 190°. All data are corrected for the effects of die entry & exit pressures (Bagley correction) and of non-Newtonian flow (Rabinowitsch correction). The shear viscosity at shear rate of 500/S, $\eta(500/S)$ is then extracted from the corrected flow curve.

1.2   **Rheotens Extensional Rheometry**

The melt strength of the polymer is measured at 190°C, using a Göttfert Rheotens extensional rheometer in conjunction with a Rosand RH 7 Capillary Rheometer. This is achieved by extruding the polymer at a constant pressure (P) through a die of 1.5 mm diameter and 30 mm in length, with a 90° entry angle.

5   Once a given extrusion pressure is selected, the piston of the capillary rheometer will travel through its 15 mm diameter barrel at a speed that is sufficient to maintain that pressure constant using the constant pressure system of the rheometer. The nominal wall shear rate ($\dot{\gamma}$) for a given extrusion pressure can then be computed for the polymer at the selected pressure.

10 The extrudate is drawn with a pair of gear wheels at an accelerating speed (V). The acceleration ranges from 0.12 to 1.2 cm/s^2 depending on the flow properties of the polymer under test. The drawing force (F) experienced by the extrudate is measured with a transducer and recorded on a chart recorder together with the drawing speed. The maximum force at break is defined as melt strength (MS) at a

15 constant extrusion pressure (P) or at its corresponding extrusion rate (γ). Three or four extrusion pressures (6, 8, 12, 16 MPa) are typically selected for each polymer depending on its flow properties. For each extrusion pressure, a minimum of 3 MS measurements are performed and an average MS value is then obtained.

        The derivative functions of the extrusion pressure and shear rate dependent

20 melt strengths, $\delta(MS)/\delta(P)$ and $\delta(MS)/\delta(\log \dot{\gamma})$, for each polymer are computed from the slopes (by a least square line fitting) of the plots of the average MS against pressure and against shear rate respectively. The melt strength and extrusion pressure at shear rate of 500 /s, (MS(500 /s), P(500 /s) respectively, were also computed from these plots. (See Figures 1-2).

25 **1.3**   **Melt Flow Rate (2.16 kg)**

        The melt flow rate (MFR) of the polymers was measured under conditions which conform to ISO 1133 (1991) and BS.2782:PART 720A:1979 procedures. The weight of polymer extruded through a die of 2.095 mm diameter, at a temperature of 190°C, during a 600 second time period and under a standard load

30 of 2.16 kg is recorded.

2   **Molecular Structure Characterisation**

        Various techniques (eg ^{13}C NMR, GPC/LALLS, GPC/intrinsic viscosity, GPC/on-line viscometry and rheological flow activation energy, etc) have been developed to indicate the presence of long chain branching in polymers.

35   **2.1**   **Molecular Weight Distribution (M_w/M_n) and Long Chain Branching**

(LCB) Measurements by GPC/on-line viscometry.

Molecular weight distribution was determined by gel permeation chromatography/on-line viscometry (GPC/OLV) using a Waters 150CV. The method followed was based upon that described by J. Lesec et al, Journal of Liquid

5 Chromatography, 17, 1029 (1994). It is well known to those skilled in the art that this technique can provide an estimate of long chain branching (LCB) content as a function of molecular weight. While it is possible to interpret the data in terms of the number of long chain branches per 1000 carbon atoms, an alternative approach is to interpret the data in terms of the parameter g' which is the ratio of the

10 measured intrinsic viscosity to that of a linear polymer having the same molecular weight. Linear molecules show g' of 1, while values less than 1 indicate the presence of LCB. As always, the reliability of LCB determinations can be greatly strengthened by combining results from several techniques rather then relying on a sole method.

15 Average values of g' were calculated from the equation $<g'>_{LCB}=[\eta]/[\eta]_{lin}$

where $[\eta] = \Sigma(w_i [\eta]_i$, and $[\eta]_{lin} = \Sigma(w_i [\eta]_{i,lin}$

where w_i is the weight fraction, $[\eta]_i$ are measured intrinsic viscosities of the long chain branched polymer fractions, and $[\eta]_{i,lin}$ are the intrinsic viscosities of the equivalent linear polymers of the same molecular weight for each slice, all

20 calculated from the slice data of the GPC/OLV experiment. The averaging was carried out over the range of molecular weight for which reliable measures of $[\eta]_i$ could be made. The data were not corrected for any contribution to g' due to short chain branching. A molecular weight distribution corrected for LCB and molecular weight averages corrected for LCB were calculated in the normal manner. For

25 some analyses of polymers known not to contain LCB the on-line viscometer was not used and uncorrected data are reported and hence for these no $< g^1 > $ LCB value is given.

Flow Activation Energy (Ea) Measurement

Rheological measurements were carried out on a Rheometrics RDS-2 with

30 25 mm diameter parallel plates in the dynamic mode. Two strain sweep (SS) experiments were initially carried out to determine the linear viscoelastic strain that would generate a torque signal which is greater than 10% of the full scale (2000 g-cm) of the transducer over the full frequency (eg 0.01 to 100 rad/s) and temperature (eg 170° to 210°C) ranges. The first SS experiment was carried out at

35 the highest test temperature (eg 210°C) with a low applied frequency of 0.1 rad/s.

This test is used to determine the sensitivity of the torque at low frequency. The second experiment was carried out at the lowest test temperature (eg 170°C) with a high applied frequency of 100 rad/s. This is to ensure that the selected applied strain is well within the linear viscoselastic region of the polymer so that the

5   oscillatory rheological measurements do not induce structural changes to the polymer during testing. This procedure was carried out for all the samples.

The bulk dynamic rheological properties (eg G', G" and η^*) of all the polymers were then measured at 170°, 190° and 210°C. At each temperature, scans were performed as a function of angular shear frequency (from 100 to 0.01

10   rad/s) at a constant shear strain appropriately determined by the above procedure.

The dynamic rheological data was then analysed using the Rheometrics RHIOS V4.4 Software. The following conditions were selected for the time-temperature (t-T) superposition and the determination of the flow activation energies (E_a) according to an Arrhenius equation, $a_T = \exp(E_a/kT)$, which relates

15   the shift factor (a_T) to E_a:

Rheological Parameters:	$G'(\omega)$, $G''(\omega)$ & $\eta^*(\omega)$
Reference Temperature:	190°C
Shift Mode:	2D (ie horizontal & vertical shifts)
Shift Accuracy:	High
Interpolation Mode:	Spline

20   The copolymers of the present invention may also be described with reference to melt flow ratio which is the ratio of I_{21}/I_2 wherein I_{21} is measured at 190°C in accordance with ASTM-D-1238 Condition E.

Copolymers according to the invention have a I_{21}/I_2 value of ≥ 35,

25   preferably ≥ 40.

Example 1 (Preparation and Use of Zr (II) polymerisation catalyst)

(i)   Treatment of silica

A suspension of Crossfield ES70 silica (20 kg, previously calcined at 500°C for 5 hours) in 110 litres of hexane was made up in a 240 litre vessel under

30   nitrogen and 3.0g of Stadis 425 (diluted in 1 litre hexane) was added. A solution of TEA in hexane (30.0 moles, 0.940M solution) was added slowly to the stirred suspension over 30 minutes, while maintaining the temperature of the suspension at 30°C. The suspension was stirred for a further 2 hours. The hexane was decanted, and the silica washed with hexane, so that the aluminium content in the final

35   washing was less than 1 mmol Al/litre. Finally the suspension was dried *in vacuo* at

60°C to give a free flowing treated silica powder.

(ii)   Production of Catalyst

Toluene dried over molecular sieves (350 ml) was added to 100g of the
treated silica powder in a large Schlenk tube in a dry nitrogen glove box. The tube

5   was shaken well to form a suspension and left to stand for 1 hour. To the
suspension was added a solution of tris(pentafluorophenyl)boron in toluene
(11.3ml, 7.85 wt. %, d = 0.88 g/ml) by syringe. Then rac ethylene bis indenyl
zirconocene 1-4 diphenyl butadiene (0.845g) was added. The suspension was
shaken well for 5 minutes, then dried *in vacuo* at ambient temperature to give a

10   free-flowing pink/red powder.

(iii)   Gas-phase Fluidised bed Production of an Ethyene/Hexene-1 Copolymer

Ethylene, hexene-1, hydrogen and nitrogen were polymerised using a 15cm
diameter continuous fluidised bed reactor system. Polymer product was removed
at regular intervals from the reactor. Operating conditions are given in Table 1. The

15   product was a white free flowing powder..

Examples 2 and 3 (Preparation and Use of Zr(II) catalysts)

(i)   Treatment of the Silica Support

110 litres of hexane was placed in a 240 litre vessel under nitrogen and 1.7
g of Stadis 425 (diluted at 1 wt. % in hexane) was added. 11 kg of ES70 Crossfield

20   silica (previously dried at 500°C for 5 hours) was then added. 16.5 moles of TEA
(0.87 mole in hexane) was then added at 30°C during a period of 30 minutes. After
a holding period of 2 hours, the hexane was decanted and the silica was washed 6
times with 130 litres of hexane.

(ii)   Production of the Catalyst

25   The silica treated as above was dried and then 38 litres of toluene added.
11.7 kg of rac ethylene bis indenyl zirconocene 1-4 diphenyl butadiene solution in
toluene (1.32wt%) was added at ambient temperature during a period of 15
minutes. 0.7 g of Stadis 425 (diluted at 1wt% in toluene) was added. The catalyst
was then dried under vacuum (4 mmHg) at 40°C to give a free flowing powder.

30   Then 2.33 kg of tris pentafluorophenyl boron solution (6.12wt% in toluene)
was added at ambient temperature during a period of 2 hours while maintaining
continuous agitation. After a holding period of 1 hour again maintaining agitation
a pink/red catalyst having residual solvent therein was obtained.

(iii)   Gas-phase Fluidised Bed Production of an Ethylene/Hexene-1 Copolymer

35   Ethylene, hexene-1, hydrogen and nitrogen were fed into a 45cm diameter

continuous fluidised bed reactor. Polymer product was continuously removed from the reactor. Operating conditions are given in Table 1:

Example 4

(i)   Treatment of silica

A suspension of ES70 silica (16 kg, previously calcined at 500°C for 5 hours) in 110 litres of hexane was made up in a 240 litre vessel under nitrogen. 1.7 g of Stadis 425 diluted in 1 L of hexane was added. A solution of TEA in hexane (24.0 moles, 1.0M solution) was added slowly to the stirred suspension over 30 minutes, while maintaining the temperature of the suspension at 30°C. The suspension was stirred for a further 2 hours. The hexane was filtered, and the silica washed with hexane, so that the aluminium content in the final washing was less than 1 mmol Al/litre. Finally the suspension was dried *in vacuo* at 60°C to give a free flowing treated silica powder.

(ii)   Catalyst fabrication

41.6L of toluene was added to the above treated silica powder. 12.67 kg of rac ethylene bis indenyl zirconocene 1-4 diphenyl butadiene solution in toluene (1.16wt%) was added at ambient temperature during a period of 15 min then kept at 25°C for 15 min. 50 ppm of Stadis 425 diluted in 1L of toluene was added. The catalyst was then dried under vacuum at 40°C to give a free flowing powder.

Then 2.22 Kg of tris(pentafluorophenyl)boron solution in toluene (6.12wt%) was added at ambient temperature during a period of 2 hours while maintaining continuous agitation After a holding period of 1h again maintaining agitation a catalyst having residual solvent therein was obtained.

(iii)   Gas Phase Fluidised bed production of an ethylene-hexene-1 copolymer

The polymerisation was carried out as for Example 1, under conditions summarised in Table 1

Example 5

(i)   Treatment of silica

26.24Kg of TEA treated ES70 silica was prepared in a dryer under nitrogen essentially as described in Example 4.

(ii)   Catalyst fabrication

10 litres of 0.0809M solution in toluene of bis(hydrogenated tallow alkyl) methyl ammonium tris(pentafluorophenyl)(4-hydroxyphenyl)borate, was mixed with 0.9 litres of TEA (1.01M) in toluene. The mixture was added to the treated silica with agitation and allowed to mix for 45 minutes. The solvent was removed

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during 1 hour under vacuum at a temperature of 31°C. 25 litres of 0.021M rac ethylene bis indenyl zirconocene 1-4 diphenyl butadiene in toluene was added and allowed to mix for 45 minutes. The solvent was removed during 105 minutes under vacuum at 34°C. The finished catalyst was steel-grey in colour and

5 contained less than 0.25% residual solvent.

(iii) <u>Gas Phase Fluidised bed production of an ethylene-hexene-1 copolymer</u>

The polymerisation was carried out as for Examples 2 and 3, under conditions summarised in Table 1

<u>Example 6</u>

10 (i) <u>Treatment of silica support</u>

A suspension of ES70 silica (16 kg, previously calcined at 500°C for 5 hours) in 110 litres of hexane was made up in a 240 litre vessel under nitrogen. 1.7g of a solution of Stadis 425 (in 1 litre of hexane) was added. A solution of TEA in hexane (24.0 moles, 0.838M solution) was added slowly to the stirred

15 suspension over 30 minutes, while maintaining the temperature of the suspension at 30°C. The suspension was stirred for a further 2 hours. The hexane was filtered, and the silica washed with hexane, so that the aluminium content in the final washing was less than 0.5 mmol Al/litre. Finally the suspension was dried *in vacuo* at 60°C to give a free flowing treated silica powder.

20 (ii) <u>Production of the Catalyst</u>

All manipulations were done under an inert nitrogen atmosphere in a dry box. To 64.5 mL of a 0.073M solution in toluene of bis(hydrogenated tallow alkyl) methyl ammonium tris(pentafluorophenyl)(4-hydroxyphenyl)borate, was added 20.8 mL of 0.25 M Et$_3$Al in toluene. 84.7 mL of this mixture was quantitatively

25 added to 150 g of treated silica in a 3 L Round bottom flask and the resulting mixture was agitated for 30min at ambient temperature. The solvent was removed under vacuum at 30°C to the point where no further evolution of volatiles was observed. Immediately after, 138.3 mL of 0.017M rac ethylene bis tetrahydro indenyl zirconocene 1-4 diphenyl butadiene in toluene were added and the powder

30 was again agitated for 30 min at ambient temperature. The solvent was removed under vacuum at ambient temperature to the point where no further evolution of volatiles was observed.

(iii) <u>Gas Phase Fluidised bed production of an ethylene-hexene-1 copolymer</u>

The polymerisation was carried out as for Example 1, under conditions

35 summarised in Table 1

Example 7

All manipulations were done under an inert nitrogen atmosphere in a dry box.

(i)   Treatment of silica

5   Twenty grams of Crosfield ES-70 silica that were calcined in air at 500 °C were accurately weighed into a 250 mL Schlenk flask. 125 mL of hexane were added to make a slurry. 30.8 mL of 1.0 M TEA in hexane were added while swirling the flask by hand and the flask was left to stand for 1 hour. The treated silica was filtered on a frit and washed with several volumes of hexane. The silica

10   was dried to constant weight under vacuum at ambient temperature. 21.7 g of treated silica were recovered

(ii)   Production of catalyst

Two grams of the above treated silica were accurately weighed into a 100 mL Schlenk flask and 8 cc of toluene were added to make a slurry. 2.4 mL of

15   0.017 M rac ethylene bis tetrahydro indenyl zirconocene 1-4 diphenyl butadiene in toluene and 0.5 mL of 0.127 M tris(pentafluorophenyl)boron were added, in that order, while swirling the flask by hand. The solvent was removed till constant weight, under vacuum at ambient temperature. 1.9 g of catalyst powder were recovered.

20   (iii)   Gas Phase production of an ethylene-hexene-1 copolymer

The polymerisation was carried out in a 2.5-litre stirred, fixed bed autoclave. This was charged with 300 g dry NaCl, and stirring was begun at 300 rpm. The reactor was pressurised to 8.39 bar ethylene that contained 500 ppm volume of hydrogen and heated to 71 °C. 1-hexene was introduced to a level of 6000 ppm volume as

25   measured on a mass spectrometer. 0.5 g of TEA was introduced into the reactor. In a separate vessel, 0.1 g catalyst was mixed with an additional 0.5 g TEA treated silica. The combined catalyst and TEA treated silica were subsequently injected into the reactor. Ethylene pressure was maintained on a feed as demand, and hexene was fed as a liquid to the reactor to maintain the ppm concentration.

30   Temperature was regulated by dual heating and cooling baths. After 180 minutes the reactor was depressurised, and the salt and polymer were removed via a dump valve. The polymer was washed with copious distilled water to remove the salt, then dried at 50 °C. 282g of a white polymer powder was recovered.

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TABLE 1

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
Total pressure (bar)	14.3	19	19	14.3	18	14.5
Temperature (°C)	70	70	70	70	65	70
C2 pressure (bar)	12	11.8	10	8	8.5	4
H2/C2	0.0005	0.0005	0.0014	0.0003	0.00056	0.0006
C6/C2	0.007	0.0061	0.0055	0.007	0.0057	0.0075
Production(Kg/h)	1.3	43	39	1	100	0.7

TABLE 2

Property Polymers	MFR (2.16 kg) (g/10 min)	Density (A) (kg/m·3)	Mw/Mn	<g>LCB	Ea (kJ/mol)	h(500/s) (Pa.s)	MS (500/s) (cN)	P (500/s) (MPa)	d(MS)/d(kog/s) (cN)	d(MS)/d(P) (cN/MPa)
Example 1	1.1	920	5.9	0.68	65.1	260	16.7	15.6	9.22	0.81
Example 2	0.3	920	5.0	0.74	74.1	290	19.3	17.5	8.62	0.85
Example 3	1.0	923	5.3	0.77	67.0	220	16.2	14.4	9.19	0.85
Example 4	0.9	920.3	5.3	0.80	65.4	240	17.7	14.7	11.10	1.04
Example 5	1.1	917.9	3.6	--	62.4	385	10.0	17.8	5.81	0.50
Example 6	1.3	921.4	3.5	--	56.7	400	6.3	18.6	4.03	0.37
Example 7	0.66	926.8	3.7	--	66.7	455	5.0	13.7	3.13	0.33
Exceed MEL27MAX	0.85	926	2.3	1.0	--	690	4.4	32.0	2.11	0.13
Exceed 350D60	1.12	917.7	2.1	--	30.8	760	4.0	31.0	1.77	0.11
Dowlex 2045	1.1	919	3.3	--	32.0	580	5.5	23.0	2.00	0.15
MOBIL NTA 101	0.84	920	3.4	--	31.0	515	4.8	25.0	2.15	0.16
LL7209AA	0.9	920	3.8	--	31.3	570	6.3	24.4	2.85	0.22
LL7206AF	0.6	920	3.9	--	31.0	600	9.5	27.0	4.19	0.33
Borealis LE6592	0.15	922.9	11.5	--	--	370	15.0	20.0	6.25	0.70
Affinity FM 1570	1.0	915	2.2	0.92	60.8	570	5.5	24.0	2.64	0.19
EBI/Zr(IV)/MAO	0.77	918.3	3.4	0.85	60.2	440	13.0	19.5	7.38	0.59
LD5320AA	2.1	921	6.8	0.59	57.8	240	14.5	12.8	11.88	1.05
LD5310AA	1.0	923	7.0	0.53	65.3	300	16.6	14.0	8.67	1.07

Film Tests

Film was produced from the product of example 2 and LD5310AA using a Collin single screw film extruder (45mm, 25L/D) equipped with an LDPE screw and using a temperature profile typical of that used for extrusion of LDPE. The
5   results are summarised in Table 3 together with results for examples 8-10 which were produced under similar catalyst and polymerisation conditions to example 2.

It can be seen that for all of the example polymers that the extrusion behaviour is improved compared to the control LDPE product as judged by their lower extrusion head pressure, lower motor load and lower specific energy. In
10   addition, this has been achieved for products with melt indices lower than the conventional LDPE ie products which might be expected to show more difficult extrusion behaviour. At the same time, mechanical properties similar to LDPE or improved have been obtained.

Similar film extrusions have been carried out for examples 5 and 6 and
15   these are reported in Table 4. For these products, the processing is less advantageous compared to LDPE, as evidenced by the values for head pressure, motor load and specific energy, but the mechanical are considerably better than LDPE and the optical properties are comparable.

Film Test Methods

20   Film dart impact was measured according to ASTM D1709, (Method A) teas strength by ASTM D1922, and tensile properties by ASTM D822. Haze was measured by ASTM D1003 and gloss by D2457.

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TABLE 3

Example		2	8	9	10	LD5310AA
Compounding						
Machine		ZSK53	ZSK58	ZSK58	ZSK58	
CaSt	ppm	1250	1250	1250	1250	
Irganox 1076	ppm	500	500	500	500	
Irgafos PEPQ	ppm	800	800	800	800	
Pellet properties						
Melt Index	g/10min	0.31	0.32	1.38	0.68	0.9
Density	Kg/m3	920	922.9	922	919.5	921
I21/I2		95	84	51	69	62
Film extrusion						
Machine		Collin	Collin	Collin	Collin	Collin
Die	mm	100	100	100	100	100
Die gap	mm	0.8	0.8	0.8	0.8	0.8
T° Profil		175/190/ 195/200/ 200/200/ 210/210	140/150/1 60/170/17 0/170/190/ 180	140/150/1 60/170/17 0/170/190/ 180	140/150/1 60/170/17 0/170/190/ 180.	140/150/1 60/170/ 170/170/1 90/180
Screw speed	rpm	40	40	41	40	45
Melt pressure	bar	151	238	166	187	245
Output	Kg/h	12	12	12	12	12
Motor Load	A	10.7	14.5	11.7	13.9	13.6
Melt Temp.	°C	190	165	161	162	163
Haul off rate	m/mn	10.2	8.8	11	9.1	10
BUR		2:1	2:1	2:1	2:1	2:1
Frostline	mm	250	160	120	350	120
Specific energy	Kwh/Kg	0.12	0.17	0.14	0.16	0.18
Film properties						
Thickness	um	38	38	38	39-41	38
Dart impact	g	160	205	103	170	140
MD tens. st. break	MPa			23.5		36
TD tens. st. break	MPa			24		25
MD elongation	%			520		350
TD elongation	%			650		710

TABLE 4

Example		LD5310AA	5	6
Compounding				
Machine			ZSK58	ZSK53
CaSt	ppm		1250	1250
Irganox 1076	ppm		500	500
Irgafos PEPQ	ppm		800	800
Pellet properties				
Melt Index	g/10min	0.85	0.52	1.29
Density	Kg/m3	921	918.3	921.4
I21/I2		61	65.4	40
Film extrusion				
Machine		Collin	Collin	Collin
Die	mm	100	100	100
Die gap	mm	0.8	0.8	0.8
T° Profil		140/150/160/170/170/170/190/180	140/150/160/170/170/170/190/180	140/150/160/170/170/170/190/180
Screw speed	rpm	44	42	42
Melt pressure	bar	224	273	297
Output	Kg/h	12	12	12
Motor Load	A	15.3	16.7	17.2
Melt Temp.	°C	155	153	157
Haul off rate	m/mn	9.6	9.6	9.3
BUR		2:1	2:1	2:1
Frostline	mm	350	350	350
Specific energy	kWh/Kg	0.19	0.20	0.21
Film properties				
Thickness	um	38	38	38
Dart impact	g	102	360	252
Haze	%	5	10.7	8.1
Gloss	o/oo	72	50	61

Claims:

1.   A copolymer of ethylene and one or more alpha olefins containing from three to twenty carbon atoms said copolymer having:-

a)   a long chain branching g' value of less than or equal to 0.9 and

b)   a value of the derivative function $\delta(MS)/\delta(P)$ of greater than 0.6 wherein MS is the melt strength of the copolymer in cN and P is the extrusion pressure of the copolymer in MPa.

2.   A copolymer as claimed in claim 1 wherein g' is less than or equal to 0.8.

3.   A copolymer as claimed in claim 1 wherein g' is in the range 0.5 to 0.9.

4.   A copolymer as claimed in claim 3 wherein g' is in the range 0.55 to 0.85.

5.   A copolymer as claimed in claim 4. wherein g' is in the range 0.65 to 0.8.

6.   A copolymer as claimed in claim 1 wherein $\delta(MS)/\delta(P)$ is greater than 0.65.

7.   A copolymer as claimed in claim 6 wherein $\delta(MS)/\delta(P)$ is greater than 0.80.

8.   A copolymer as claimed in claim 6 wherein $\delta(MS)/\delta(P)$ is in the range greater than 0.65 to less than 1.4.

9.   A. copolymer as claimed in claim 6 wherein $\delta(MS)/\delta(P)$ is in the range from 0.8 to 1.2.

10.   A copolymer of ethylene and one or more alpha olefins containing from three to twenty carbon atoms said copolymer having:

a)   a long chain branching g' value of less than or equal to 0.9 and

b)   a value of the derivative function $\delta(MS)/\delta(\log\dot{\gamma})$ of greater than 7.5 wherein MS is the melt strength of the copolymer in cN and $\dot{\gamma}$ is the shear rate of the copolymer in secs^{-1}.

11.   A copolymer as claimed in claim 10 wherein g' is less than or equal to 0.8

12.   A copolymer as claimed in claim 10 wherein g' is in the range 0.5 to 0.9.

13.   A copolymer as claimed in claim 12 wherein g' is in the range 0.55 to 0.85.

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14. A copolymer as claimed in claim 13. wherein g' is in the range 0.65 to 0.8.

15. A copolymer as claimed in claim 10 wherein $\delta(MS)/\delta(\log\dot{\gamma})$ is greater than 8.0.

16. A copolymer as claimed in claim 10 wherein $\delta(MS)/\delta(\log\dot{\gamma})$ is from 8.0 to 12.0.

17. A homopolymer of ethylene or a copolymer of ethylene and one or more alpha olefins containing from three to twenty carbon atoms said homopolymer or copolymer having:

a)   a value of the derivative function $\delta(MS)/\delta(P)$ of greater than 0.6 and

b)   an M_w/M_n value of in the case of the copolymer less than 8 and in the case of the homopolymer less than 6 wherein MS is the melt strength of the copolymer or homopolymer in cN and P is the extrusion pressure of the copolymer or homopolymer in MPa and M_w/M_n is the ratio of weight average molecular weight to number average molecular weight of the copolymer or homopolymer as measured by gel permeation chromatography.

18. A homopolymer or copolymer as claimed in claim 17 wherein $\delta(MS)/\delta(P)$ is greater than 0.8.

19. A homopolymer or copolymer as claimed in claim 18 wherein $\delta(MS)/\delta(P)$ is greater than 0.75.

20. A homopolymer or copolymer as claimed in claim 17 wherein $\delta(MS)/\delta(P)$ is in the range greater than 0.8 to 1.2.

21. A homopolymer or copolymer as claimed in claim 17 wherein the M_w/M_n value is less than 6.

22. A homopolymer of ethylene or a copolymer of ethylene and one or more alpha olefins containing from three to twenty carbon atoms said homopolymer or copolymer having:

a)   a value of the derivative function $\delta(MS)/\delta(\log\dot{\gamma})$ of greater than 7.5 and

b)   an M_w/M_n value of less than 6.5

wherein MS is the melt strength of the copolymer in cN and γ is the shear rate of the copolymer in $secs^{-1}$ and M_w/M_n is the ratio of weight average molecular weight to number average molecular weight as measured by gel permeation chromatography.

23. A homopolymer or copolymer as claimed in claim 22 wherein $\delta(MS)/\delta(\log\dot{\gamma})$ is greater than 8.0

24. A homopolymer or copolymer as claimed in claim 22 wherein $\delta(MS)/\delta(\log\dot{\gamma})$ is from 8.0 to 12.0.

25. A homopolymer of ethylene or a copolymer of ethylene and one or more alpha olefins containing from three to twenty carbon atoms said homopolymer or copolymer having a long chain branching g' value of between about 0.6 and about 0.9.

5 26. A homopolymer or copolymer as claimed in claim 25 wherein g' is from 0.65 to 0.8.

27. A copolymer of ethylene and one or more alpha-olefins containing from three to twenty carbon atoms said copolymer having:

(a) a long chain branching g' value of less than or equal to 0.9 and

10 (b) a value of the derivative function $\delta(MS)/\delta(\log \dot\gamma)$ and a Mw/Mn satisfy the relationship:

$$\log [\delta(MS)/\delta(\log \dot\gamma)] \geq 0.6 \log (Mw/Mn) + 0.3$$

wherein Mw/Mn is the ratio of weight average molecular weight to number molecular weight as measured by gel chromatography.

15 28. A copolymer of ethylene and one or more alpha-olefins containing from three to twenty carbon atoms said copolymer having:

(a) a long chain branching g' value of less than or equal to 0.9 and

(b) a value of the derivative function $\delta(MS)/\delta(P)$ and Mw/Mn which satisfy the relationship:

20 $$\delta(MS)/\delta(P) \geq 0.12 \, Mw/Mn$$

wherein Mw/Mn is the ratio of weight average molecular weight to number molecular weight as measured by gel chromatography.

29. A copolymer of ethylene and one or more alpha-olefins containing from three to twenty carbon atoms said copolymer having:

25 (a) an flow activation energy, Ea, of value greater than or equal to 40 kJ/mol and

(b) a value of the derivative function $\delta(MS)/\delta(\log \dot\gamma)$ and a Mw/Mn which satisfy the relationship:

$$\log [\delta(MS)/\delta(\log \dot\gamma)] \geq 0.6 \log (Mw/Mn) + 0.3$$

30 wherein Mw/Mn is the ratio of weight average molecular weight to number molecular weight as measured by gel chromatography.

30. A copolymer of ethylene and one or more alpha-olefins containing from three to twenty carbon atoms said copolymer having:

(a) an flow activation energy, Ea, of value greater than or equal to 40

35 kJ/mol and

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(b) a value of the derivative function $\delta(MS)/\delta(P)$ and Mw/Mn which satisfy the relationship:

$$\delta(MS)/\delta(P) \geq 0.12 \text{ Mw/Mn}$$

wherein Mw/Mn is the ratio of weight average molecular weight to number

5   molecular weight as measured by gel chromatography.

31.   A copolymer of ethylene and one or more alpha-olefins containing from three to twenty carbon atoms said copolymer having:

(a)   a long chain branching g' value of less than or equal to 0.9 and

(b)   a value of the derivative function $\delta(MS)/\delta(P)$ and a flow activation energy

10   Ea satisfy the relationship:

$$\text{Log } [\delta(MS)/\delta(P)] \geq 3.7 - 2.4 \log (Ea)$$

wherein Ea is measured by dynamic rheometry.

32.   A copolymer of ethylene and one or more alpha-olefins containing from three to twenty carbon atoms said copolymer having:

15   (a)   a long chain branching g' value of less than or equal to 0.9 and

(b)   a value of the derivative function $\delta(MS)/\delta(\log\dot{\gamma})$ and a flow activation energy Ea satisfy the relationship:

$$\text{Log } [\delta(MS)/\delta(\log\dot{\gamma})] \geq 2.75 - 1.25 \log(Ea)$$

wherein Ea is measured by dynamic rheometry.

20   33.   A homopolymer or copolymer as claimed in any one of claims 1, 10, 17, 22, 25, 27-32 obtainable by continuously polymerising ethylene alone or with one or more alpha olefins having from three to twenty carbon atoms in the gas phase in a single reactor containing a fluidised bed of polymer particles said polymerisation being carried out in the presence of a single metallocene catalyst.

25   34.   A homopolymer or copolymer as claimed in claim 33 obtainable by continuously polymerising ethylene alone or with one ore more alpha olefins having from three to twenty carbon atoms in the gas phase in a reaction system comprising a single reactor containing a fluidised bed of polymer particles, a recycle loop connecting the inlet and outlet of the reactor and means for withdrawing the

30   homopolymer or copolymer either continuously or periodically from the reactor whilst polymerisation is occurring, said polymerisation being carried out in the presence of a single metallocene catalyst.

35.   A homopolymer or copolymer as claimed in 33 or claim 34 obtainable by continuously polymerising ethylene alone or with one or more alpha olefins having

35   from three to twenty carbon atoms in the gas phase in a single reactor containing a

fluidised bed of polymer particles said polymerisation being carried out in the presence of a single metallocene catalyst having the following general formula:

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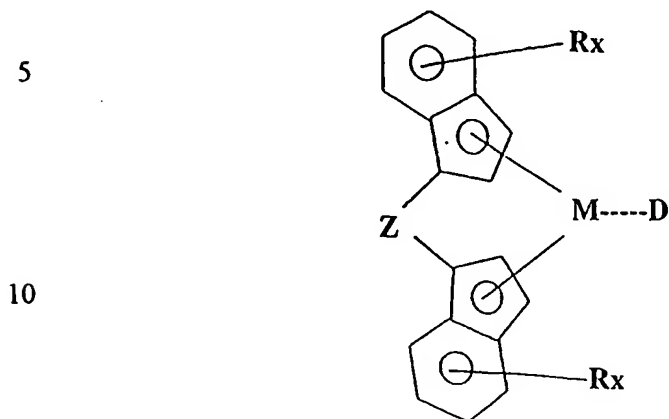
wherein

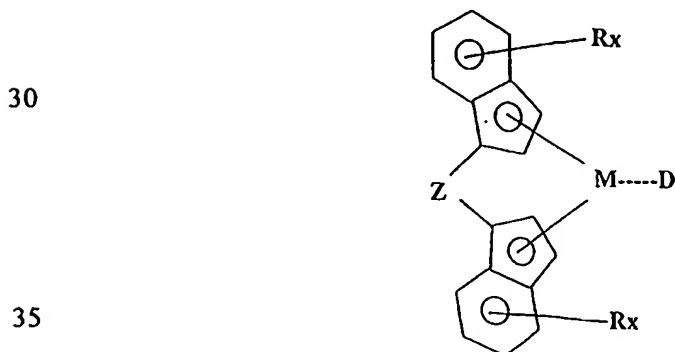15   M is titanium, zirconium or hafnium,

D is a stable conjugated diene optionally substituted with one or more hydrocarbyl groups, silyl groups, hydrocarbylsilyl groups, silylhydrocarbyl groups or mixtures thereof, said D having from 4 to 40 non-hydrogen atoms and forming a π- complex with M,

20   Z is a bridging group comprising an alkylene group having 1-20 carbon atoms or a dialkyl silyl- or germanyl group or alkyl phosphine or amino radical,

R is hydrogen or alkyl having from 1 to 10 carbon atoms and x is 1-6.

36.   A homopolymer or copolymer as claimed in 33 or claim 34 obtainable by continuously polymerising ethylene alone or with one or more alpha olefins having

25   from three to twenty carbon atoms in the gas phase in a single reactor containing a fluidised bed of polymer particles said polymerisation being carried out in the presence of a single metallocene catalyst having the following general formula:

30

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wherein

M is titanium, zirconium or hafnium in the +2 oxidation state,

D is a stable conjugated diene selected from the group consisting of s-trans-η^4,4-diphenyl-1,3-butadiene; s-trans-η^4-3-methyl-1,3-pentadiene; s-trans-η^4-1,4-dibenzyl-1,3-butadiene; s-trans-η^4-2,4-hexadiene; s-trans-η^4-1,4-ditolyl-1,3-butadiene; s-trans-η^4-1,4-bis(trimethylsilyl)-1,3-butadiene; scis-η^4- 1,4-diphenyl-1,3-butadiene; s-cis-η^4-3-methyl-1,3-pentadiene; s-cis-η^4-2,4-hexadiene; s-cis-$\eta^4$2,4-hexadiene; s-cis-$\eta^4$1,3-pentadiene; s-cis-η^4-1,4-ditolyl-1,3-butadiene; and s-cis-η^4-1,4-bis(trimethylsilyl)-1,3-butadiene, said s-cis diene group forming a π-complex as defined herein with the metal.

Z is a bridging group comprising an alkylene group having 1-20 carbon atoms or a dialkyl silyl- or germanyl group or alkyl phosphine or amino radical,

R is hydrogen or alkyl having from 1 to 10 carbon atoms and x is 1-6.

37.   A homopolymer or copolymer as claimed in 33 or claim 34 obtainable by continuously polymerising ethylene and, in the case of copolymerising, one ore more alpha olefins having from three to twenty carbon atoms in the gas phase in a single reactor containing a fluidised bed of polymer particles said polymerisation being carried out in the presence of a single metallocene catalyst having the following formula:
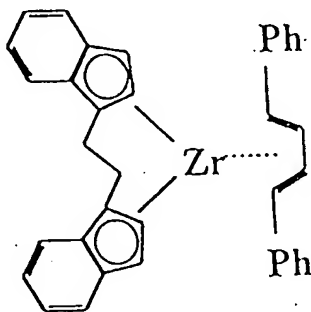
38.   A film exhibiting a dart impact value measured by ASTM D-1709 (Method A) in the range about greater than 100 and up to about 2000 comprising a copolymer as claimed in claims 1,10,17,22,25, 27-32.

39.   A film exhibiting a dart impact value measured by ASTM-D1709 (Method A) in the range about greater than 100 and up to about 2000 comprising a

copolymer of ethylene and an alpha-olefin of from 3 to 10 carbon atoms which has a density of from 0.910 - 0.930, a I_{21}/I_2 value of $\geq$ 35,.a long chain branching g^1 value of less than or equal to 0.9 and a value of the derivative function $\delta(MS)/\delta(P)$ of greater than 0.6.

5   40.   A film exhibiting a dart impact value measured by ASTM-D1709 (Method A) in the range about greater than 100 and up to about 2000 comprising a copolymer of ethylene and an alpha-olefin of from 3 to 10 carbon atoms which has a density of from 0.910 - 0.930, a I_{21}/I_2 value of $\geq$ 35,.a long chain branching g^1 value of less than or equal to 0.9 and a value of the derivatie function $\delta(MS)/\delta(P)$

10   and flow activation energy Ea satisfy the relationship

$$\log [\delta(MS)/\delta(P)] \geq 3.7 - 2.4 \log (Ea).$$

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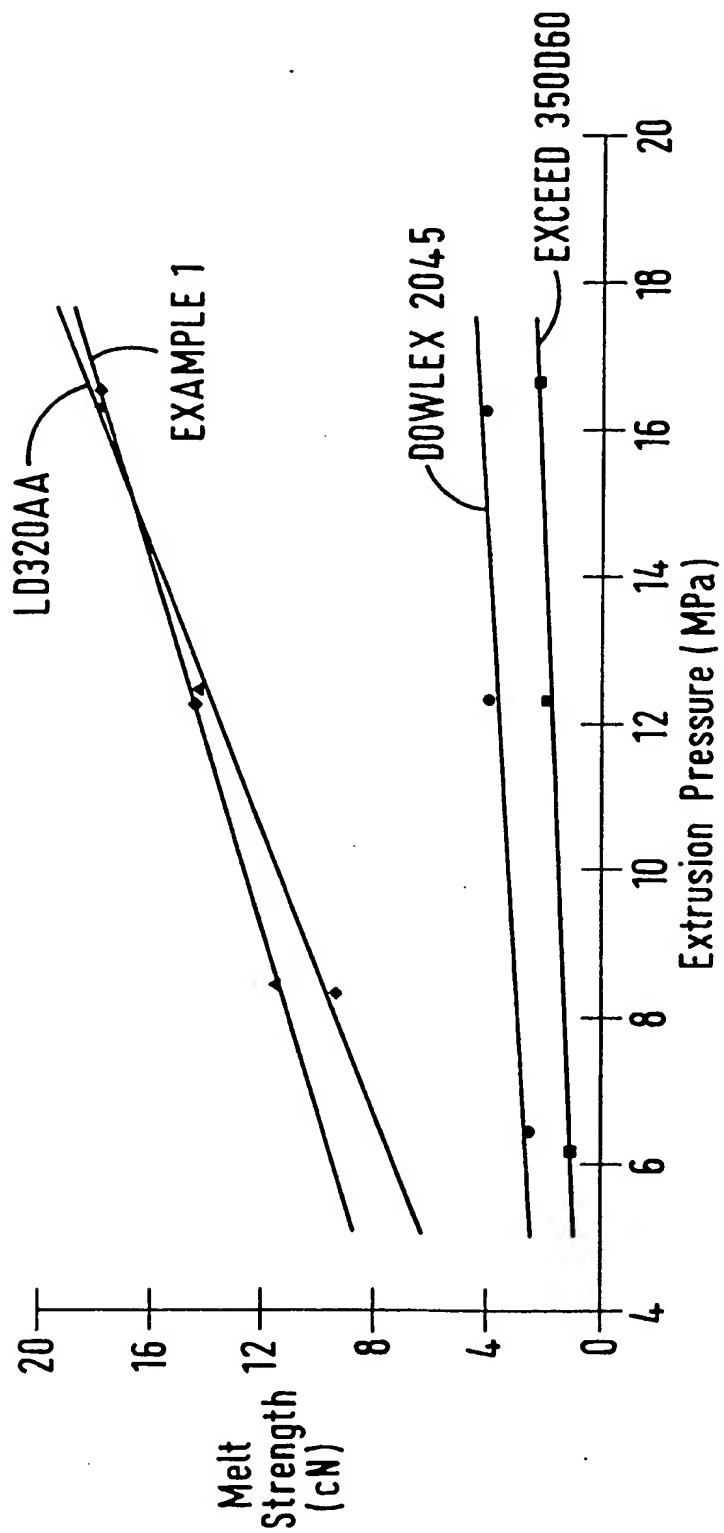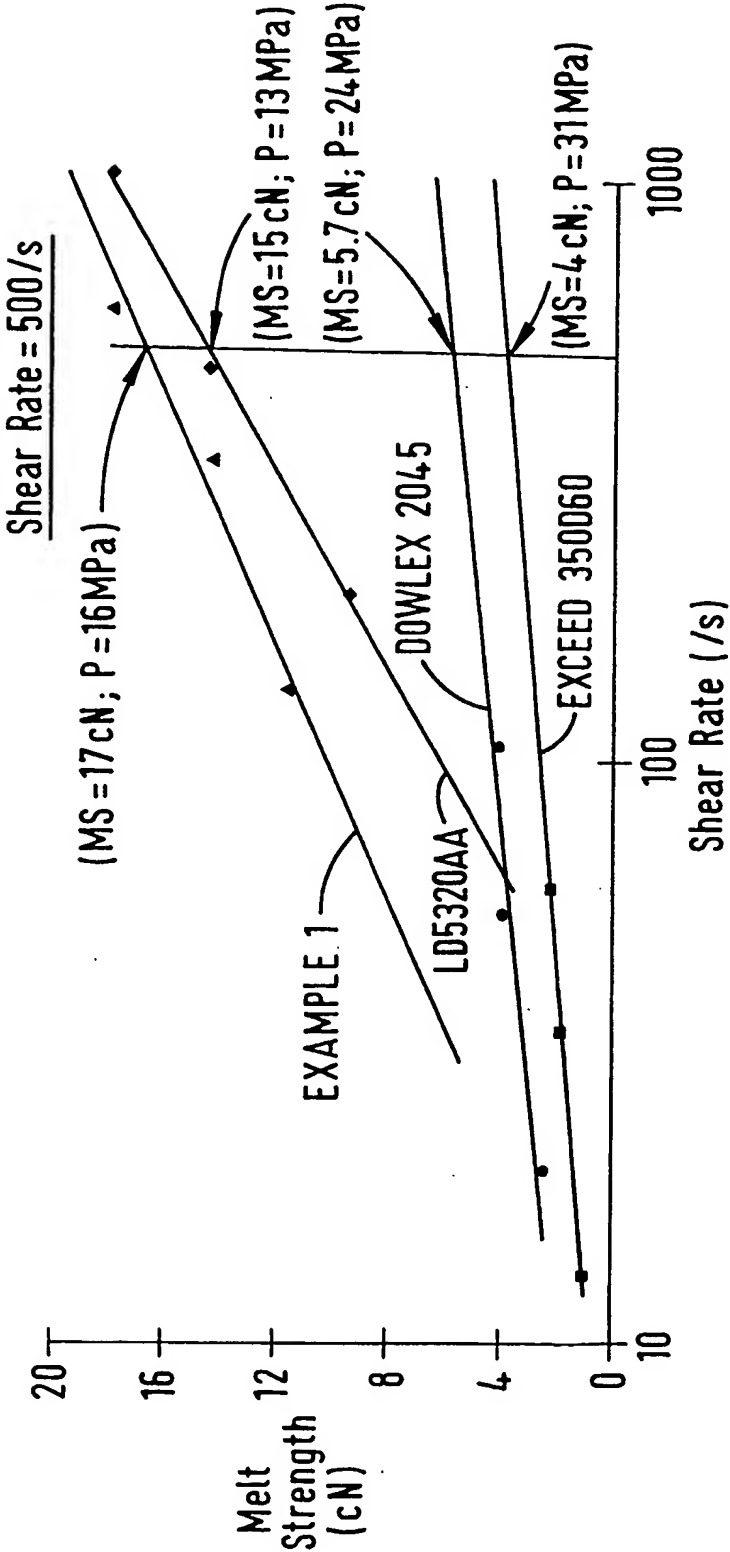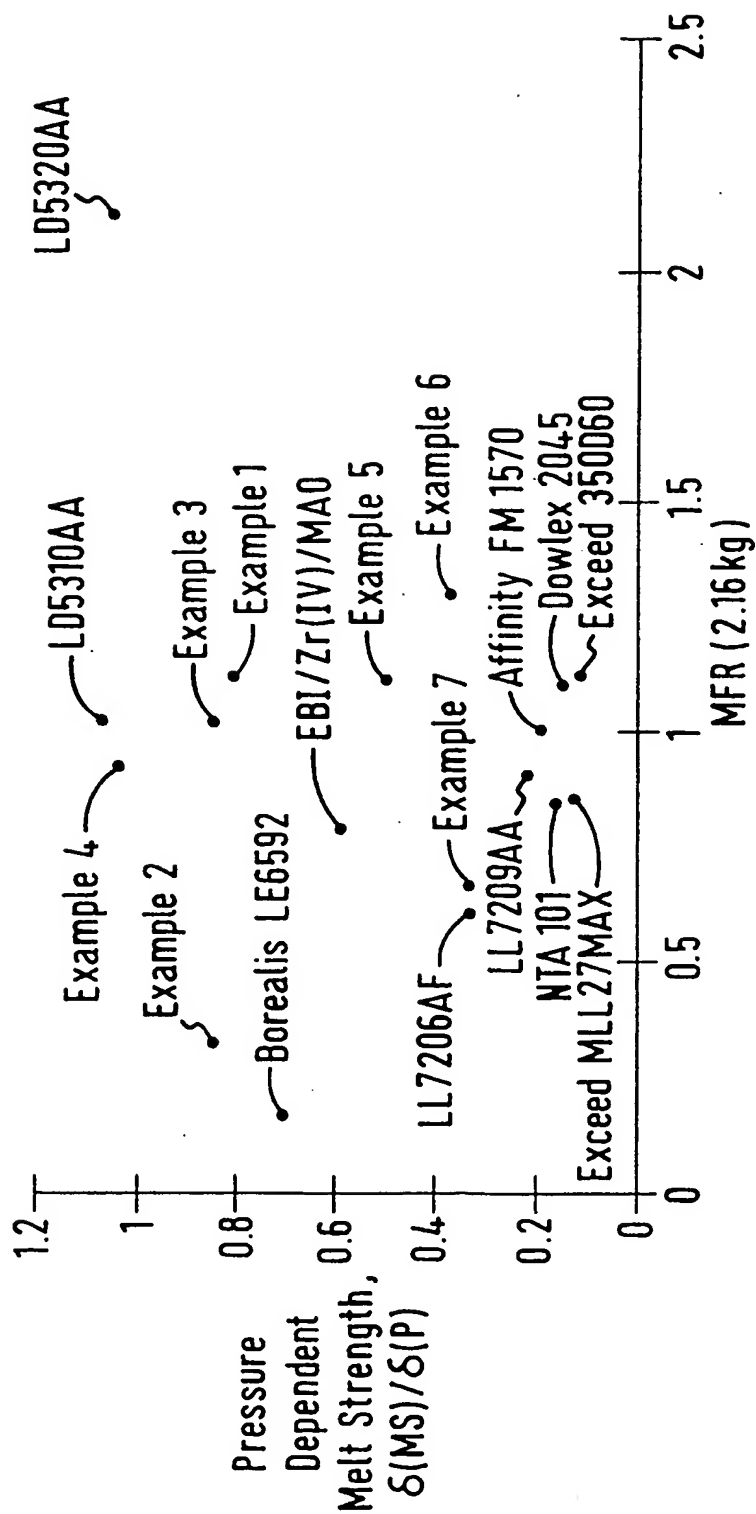

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FIG.1   PROCESSABILITY: Melt Strength at 190°C

FIG. 2   PROCESSABILITY: Melt Strength 190°C

FIG.3   Pressure Dependent Melt Strength vs MFR at 190°C

FIG.4   Shear Rate Dependent MS vs MFR at 190°C
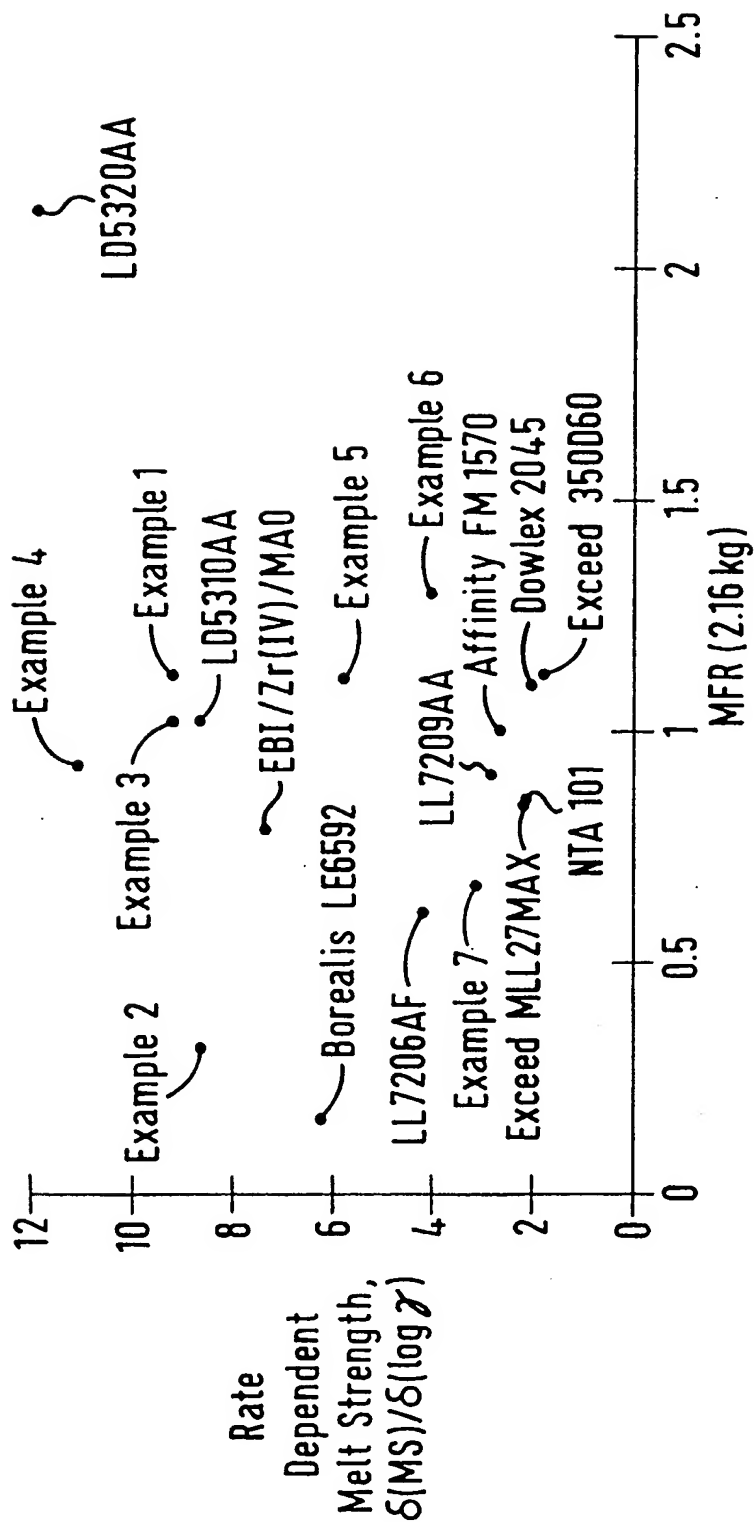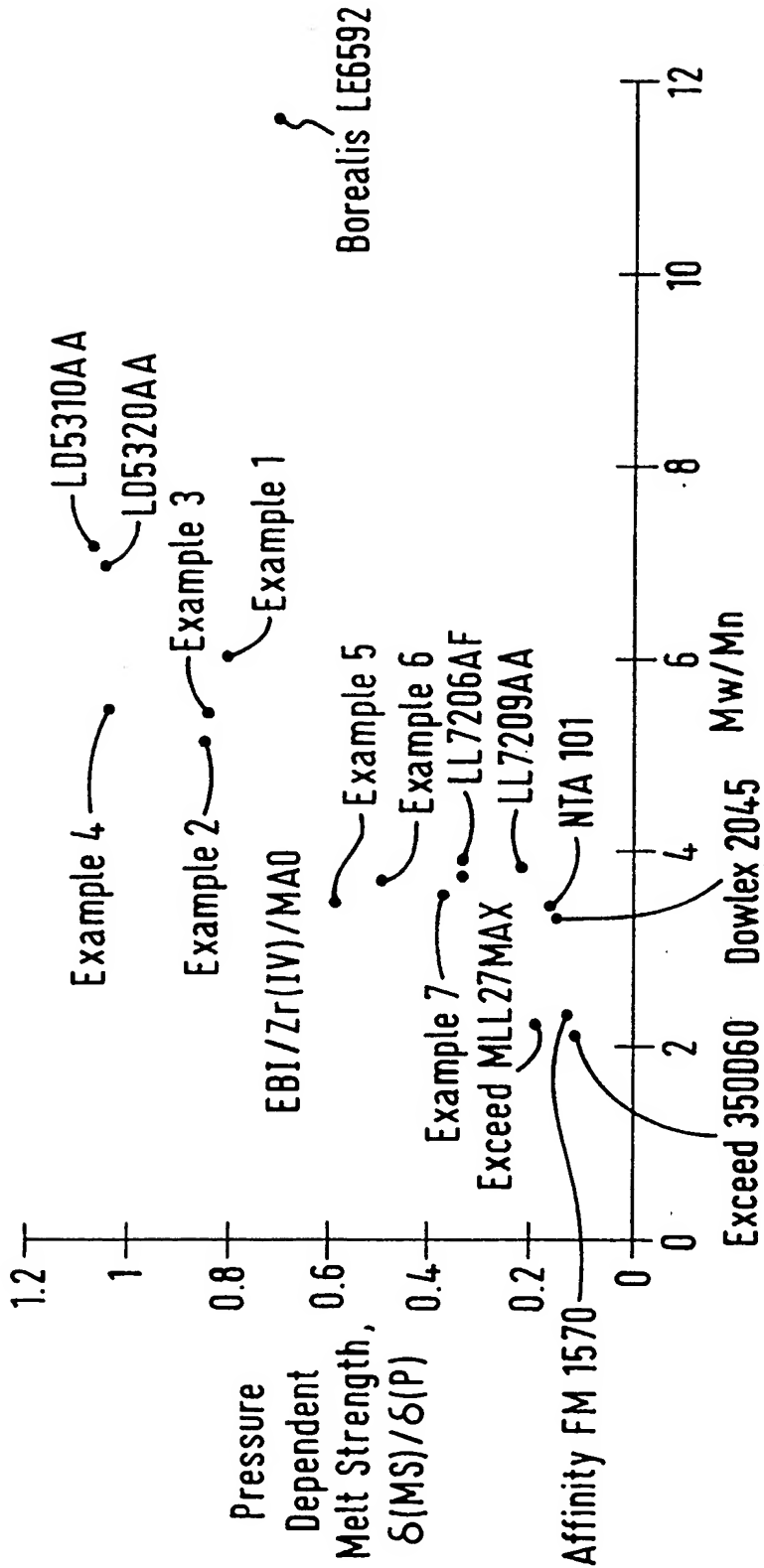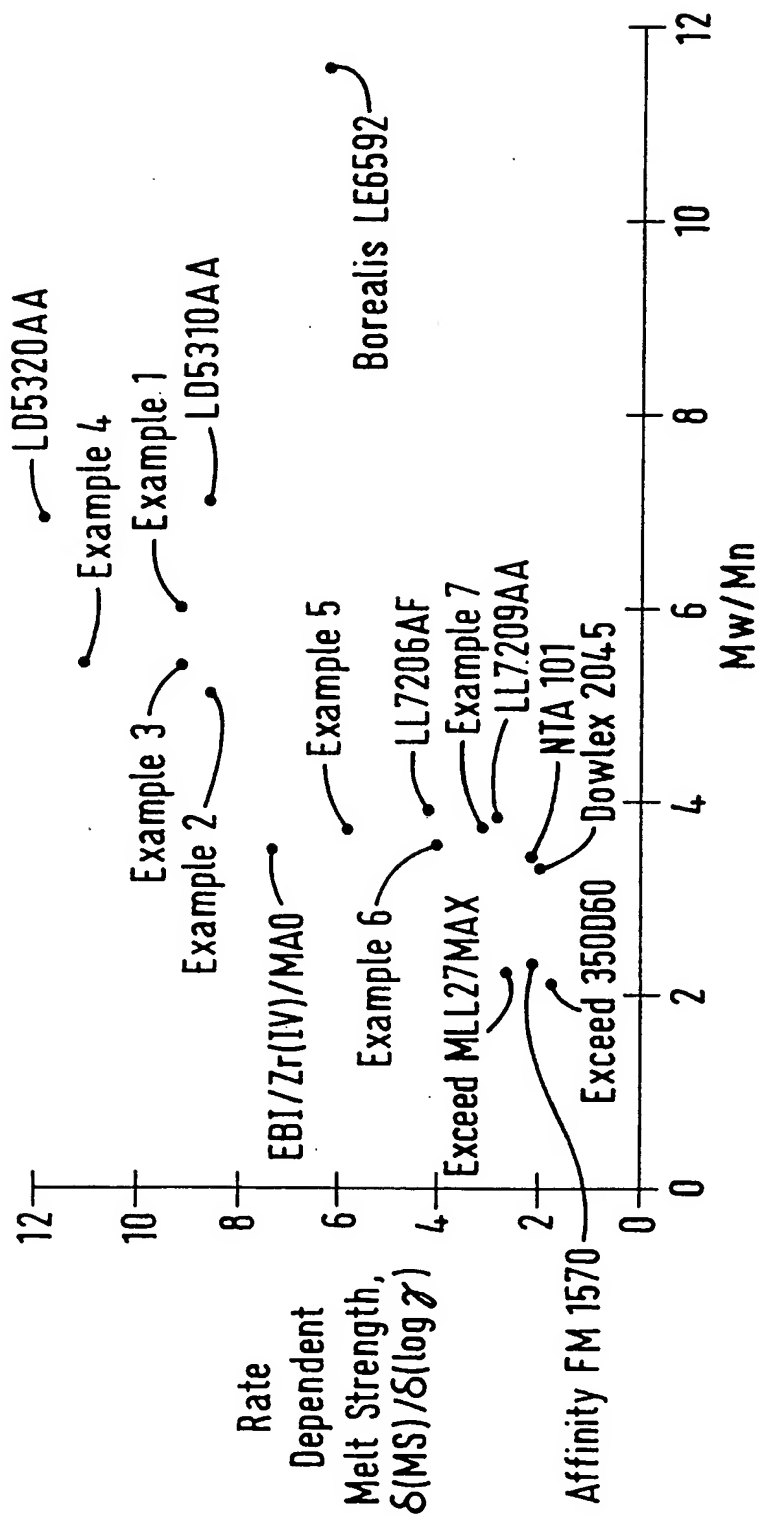
FIG.5   Pressure Dependent Melt Strength
                  vs MWD at 190°C
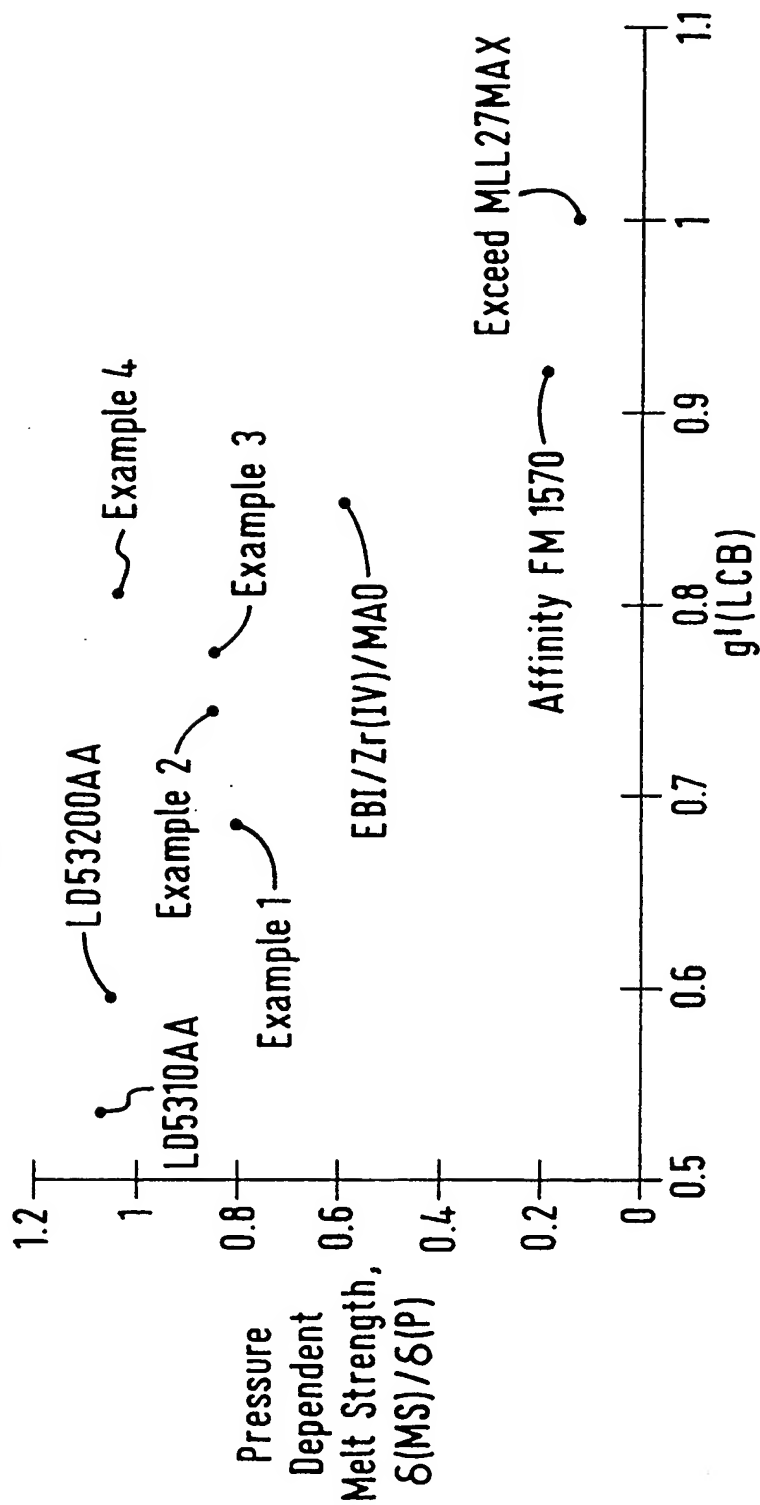
FIG.6   Shear Rate Dependent Melt Strength vs MWD at 190°C
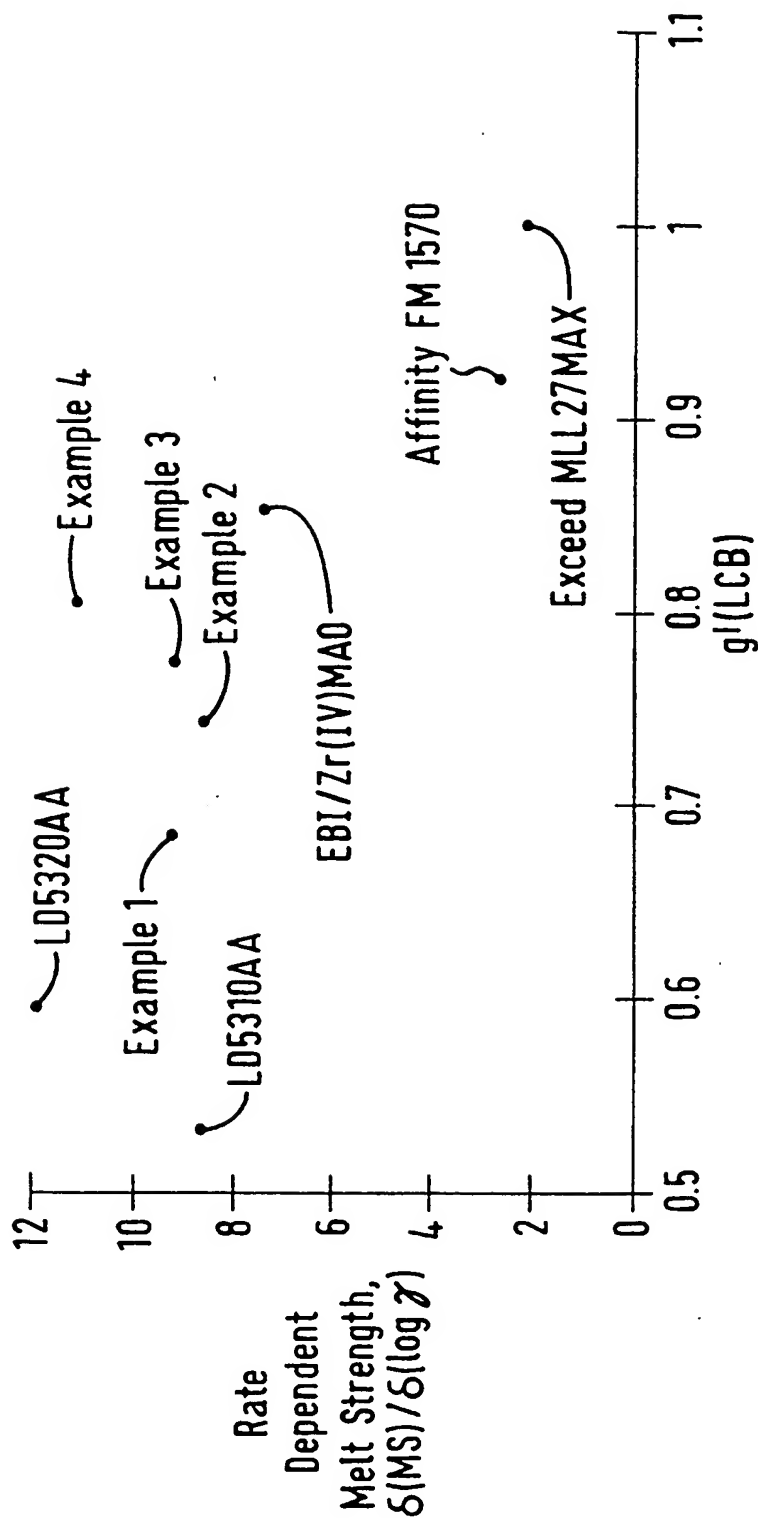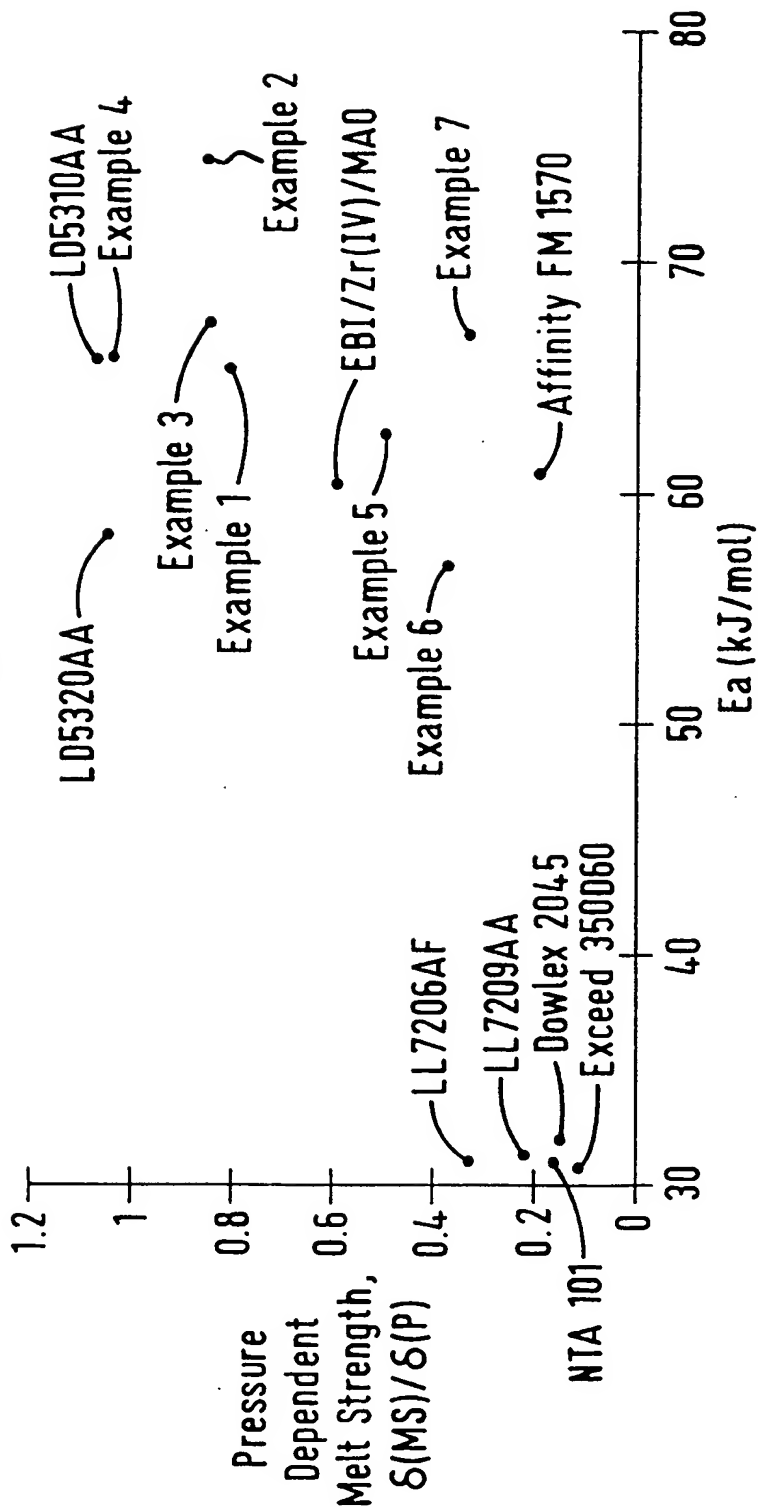
FIG.7   Pressure Dependent Melt Strength vs g'(LCB) at 190°C

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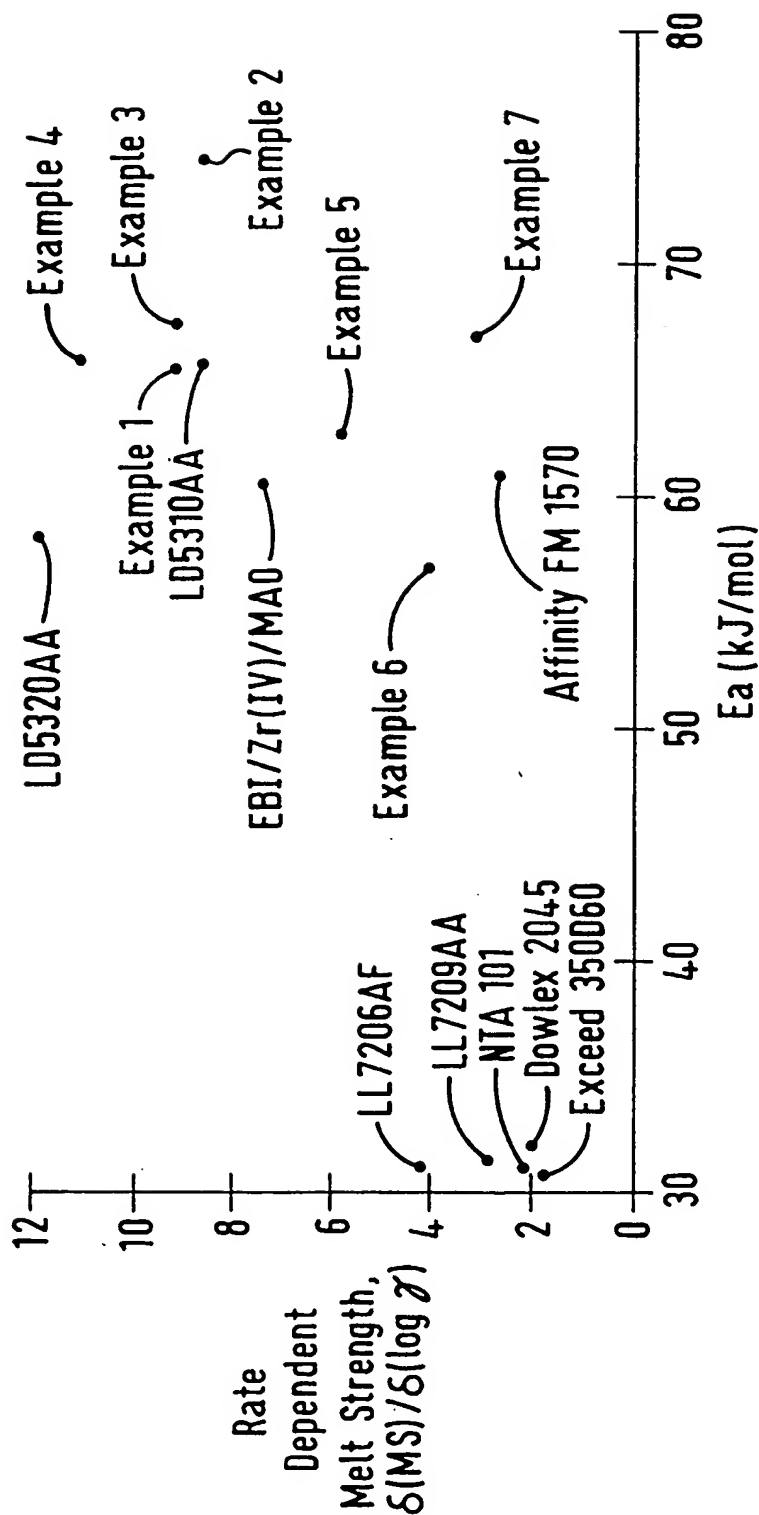
FIG. 8   Shear Rate Dependent Melt Strength
vs g'(LCB) at 190°C

FIG. 9   Pressure Dependent Melt Strength vs Flow Activation Energy (Ea) at 190°C

FIG.10   Shear Rate Dependent Melt Strength vs Flow Activation Energy (Ea) at 190°C

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6   C08F10/02   C08F4/643   C08J5/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6   C08F   C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
19 April 1999	06/05/1999

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category°	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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X	WO 96 07680 A (WILSON JOHN R ;CHUM PAK WING S (US); DOW CHEMICAL CO (US); KNIGHT) 14 March 1996 see page 31, line 1 - page 35, line 17 see page 40, line 1 - page 42, line 15 ---	1-32, 38-40
X	WO 95 04761 A (EXXON CHEMICAL PATENTS INC) 16 February 1995 see page 44; table 1 see page 47; table 4 see page 49; table 5 ---	38-40
X	US 4 642 328 A (MORTEROL FREDERIC ET AL) 10 February 1987 see example 1 ---	25
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